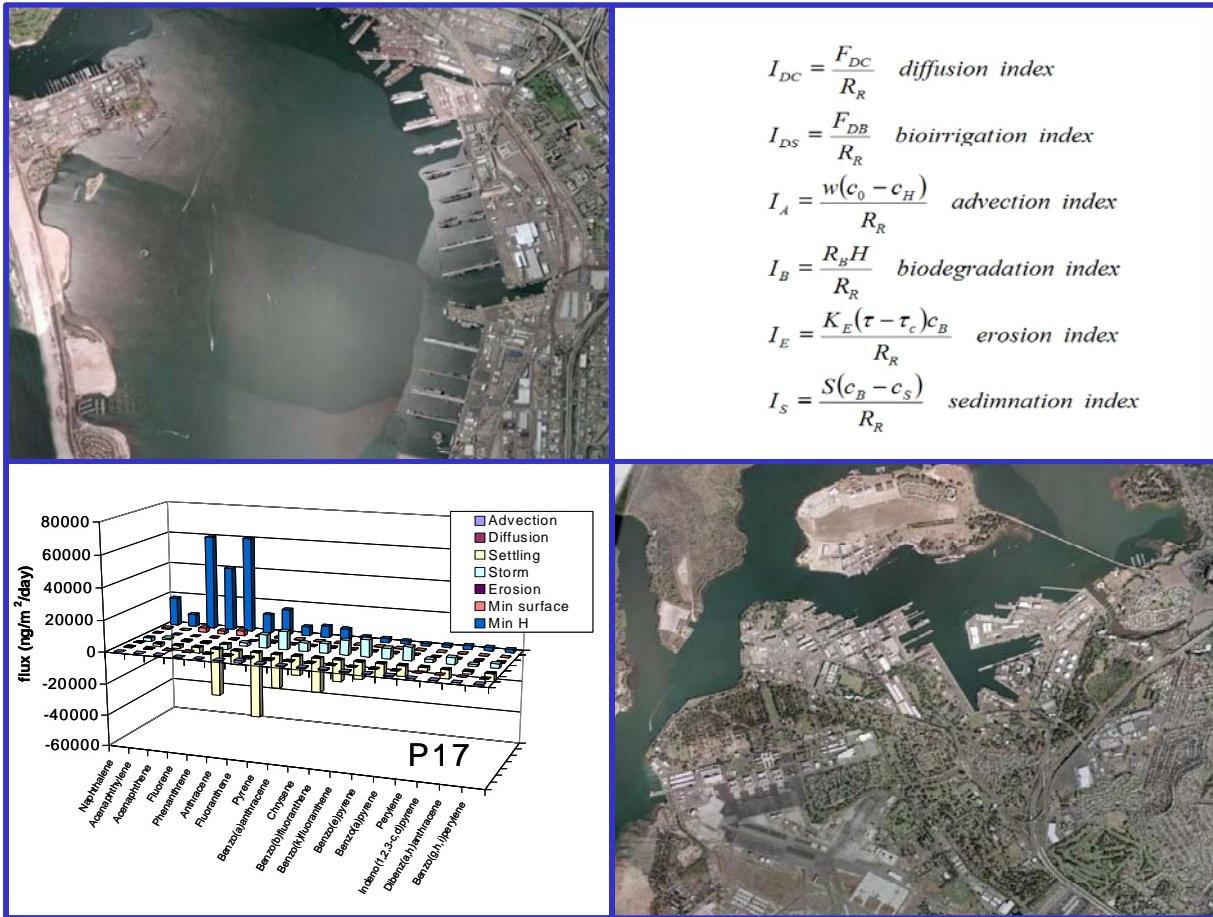


# Pathway Ranking for In-place Sediment Management (CU1209)

## Volume III: Cross-Site Comparisons

April 2006



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## **1 Objective**

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The objective of this program was to provide an understanding of the relative importance of critical pathways contaminant transport across the sediment/seawater interface in the risk, fate and management of near-shore, in-place contaminated sediments via: 1) An integrated suite of measurement techniques to characterize and quantify important transport pathways for in-place sediments, 2) A corresponding set of indices that quantify the transport phenomenon on a common dimensional scale and 3) Field scale evaluation of the effectiveness of the measurement tools and the importance of quantified transport pathways. This program consisted of two field demonstrations, the first at Paleta Creek in San Diego Bay, California, and the second at Southeast Loch and Bishop Point in Pearl Harbor, Hawaii. The detailed methods, results, and analyses for the two field studies can be found in Volume I and Volume II of this report, respectively. This final volume summarizes and compares the main results of the field efforts, and critically analyzes their implications for pathway analysis and ranking as a future tool in contaminated sediment management.

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## **2 Cross-Site Comparison of Fluxes for PRISM Pathways**

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## **2.1 PATHWAY ANALYSIS**

Analysis for PRISM Sites contained the following elements: 1) Evaluation of conceptual model, 2) evaluation of available site data, 3) field design, 4) field deployment and synthesis of field data immediately available (screening and SPI results), 5) analytical results, 6) process-specific analysis (evaluation of BFSD, flume, etc. on their own), 8) synthesis of results in terms of the field site, and 9) evaluation of results in terms of management/contaminant behavior insight. Here we present the process-specific analyses, along with analysis of the variability associated with each flux estimate.

Quantification of contaminant transport pathways in common terms is an essential element of sediment management. The PRISM approach for evaluating various pathways of contaminant flux to or from the surface sediment layer is to carry out a field-based assessment on a common scale to aid in the evaluation of risks and mechanisms of recovery or exposure to aid in management strategies. To achieve this, a measurement framework was developed that is tied to a classical 1D vertical mass balance model for the transport of contaminants in sediments. Mobility is then quantified as a net flux from the “active” surface layer. Changes in this layer result from the balance of fluxes through the defined pathways of mobility.

To achieve this, an active sediment layer of depth H is treated as a box from which contaminants can flux in or out. The results from each pathway evaluation are converted to fluxes, and all fluxes are calculated in common units. For each contaminant (16 PAHs, 9 metals), fluxes are then compared. Based upon results, dominant pathways can be determined, further site-specific studies can be recommended, the most sensitive or critical measures can be further evaluated and management approaches can be prioritized.

There are assumptions and uncertainties inherent in this approach. It is assumed that in spite of spatial and temporal variability, field measures, even if “noisy” provide insight no theoretical model can. Integration and synthesis of field-based indices forces an acknowledgement of the variability present in natural sediment systems. Integrating information from multiple field measurements makes clear the variability and heterogeneity of sediment systems in a way that no theoretical model can. While this can seem unsettling when one is used to seeing tight, modeled parameters, this is not a problem with the measurements, but an accurate reflection of the reality environmental managers face. Quantification of rates and variability provide bounds for modeling the uncertainty associated with various sediment management strategies. Thus, it is assumed that no study or approach for determining the fate and behavior of contaminants in complex systems is perfect and that intelligent users of data will apply insights into the strengths and weaknesses of this and other approaches to strike a balance between models, field data and controlled studies to inform decisions. It is the relative rates and directions of fluxes, and the management question that is applied that determine to what extent any flux represents risk and/or recovery potential. Thus, as with other types of studies, results will be applied in various ways depending upon the site and the questions being asked.

## **2.2 BIOTURBATION DEPTH**

All fluxes were evaluated relative to an active sediment layer of depth H. The bioturbation depth at a given site was used to establish the depth of H, and all further calculations used this H value. The approach for determining bioturbation depth was to use the REMOTS Sediment Profile Imager (SPI) to take in-place images throughout area, and at high density in study sites. Standard methods (Rhodes and Germano, 1982) were then used to estimate the “bio-active” layer depth based on on-site analysis of feeding void depth in SPI images. This depth scale was then used as the common depth (H) for sampling and data synthesis for most processes. There are a number of assumptions inherent in this approach. It was assumed that the bio-active mixing depth scale (H) is represented by the depth of visible feeding voids in replicate images at the site. For PRISM, it was assumed that high-density SPI images provide a means of quantifying variability and heterogeneity at a given site. This measure does not evaluate a specific flux, but provides a depth scale, as well as insight into the scale and nature of biological activity. It is assumed that the effects of bioturbation on contaminant fluxes (whether diffusive, advective or from resuspension) are embedded in other field measurements of flux.

SPI images were analyzed on-site to provide estimates of “active” mixing depths. Contrast between the surface oxidized layer and underlying anoxic sediments was also assessed to estimate the Redox Penetration Depth (RPD) (Table 2-1; Figure 2-1). In general, both the mean biological mixing depth and the mean RPD were deeper at the Pearl Harbor sites compared to the San Diego sites. Spatial variability was also generally higher at the Pearl Harbor sites. In fact, one of the main results from the PRISM project's field investigations was the spatial heterogeneity in community types and bioturbation depths documented by the SPI survey; while detailed investigations were carried out by other PRISM investigators at two selected locations within the site, the SPI results highlighted the limits to which those site-specific results could be extrapolated.

Another particularly revealing aspect of this sediment profile imaging investigation came from the time-lapse imaging at one station in each of the areas surveyed in Pearl Harbor (Figure 2-2). The results from these two deployments provided new insights into both the difference in bioturbation rates and associated processes occurring at these locations as well as the interpretation of different structures in the static “replicate images” taken as part of the regional survey. While the regular “regional survey” provided valuable information on the 3-dimensional spatial heterogeneity at the two sites, the time-lapse deployments provided insights for the first time on the fourth dimensional temporal heterogeneity -- the potential variation in reworking depths, reworking rates, and particle advection/ sediment transport that can occur at one location over a 24-hour period. For example, at Bishop Point it was found that, while large sub-surface feeding voids were present, there was virtually no temporal change in void structure, no evidence of upward particle flux, and not much evidence of subsurface activity below 2 cm. The top 2 cm, on the other hand, were a virtual hotbed of movement from surface detritus and deposit feeders. Given the high density of animals and their high rate of activity, the porewater exchange rate is most likely substantial, but the depth over which the exchange was occurring was quite shallow.

In contrast, the time-lapse profile at Station B in SE Loch showed quite dramatic changes in subsurface feeding void/burrow structure over time. The size of the three main sub-surface voids changed quite rapidly and frequently over the 24-hour recording period, and plumes of suspended sediment could periodically be seen being ejected from the main burrow. It was quite obvious that a substantial volume of sediment was being reworked down to depths of 15 cm or more, with active movement of both porewater and sediment particles throughout the entire vertical interval. The dramatic effects of crustaceans such as ghost shrimp and stomatopods on community structure and sediment properties have been documented in the past (e.g., Ott et al., 1976; Pemberton et al., 1976; Myers, 1979; Ziebis et al., 1996), and similar processes appear to be in action at much of the area in SE Loch. Because the ghost shrimp homogenize the sub-surface sediment so completely and rapidly (with voids/burrows quickly appearing and disappearing), the sediment is undergoing almost constant “roto-tilling” down to a depth of 15 cm or more. This causes this upper 20 cm of sediment to have extremely low shear strength and high water content, making it impossible for many of the sub-surface voids to remain structurally intact for any period of time. Even though the sediments in this site were subjected to more bioturbation and to a greater depth than those at Bishop Point, the information from the static profile images would have led to the opposite conclusion because of the more consolidated nature of the sub-surface sediments at Bishop Point. The subsurface feeding voids at Bishop Point were better preserved and therefore more frequent and obvious in the sediment profile images from the spatial characterization survey. The difference in the time-lapse results at the two sites also helps explain why the investigators looking at groundwater flux in these two sites saw so much more “bioirrigation noise” in their measurements at SE Loch as compared with Bishop Point.

Table 2-1. Summary of on-site determination of RPD and visual bioturbation depth.

<b>Site</b>	<b>Station</b>	<b>RPD (cm)</b>	<b>Bioturbation Depth (cm)</b>
Paleta Creek	P04	1.86±0.47	8.61±2.73
	P17	1.00±0.38	5.62±1.80
Pearl Harbor	BP	2.90±1.08	9.86±2.66
	SE	3.87±1.40	12.21±4.58

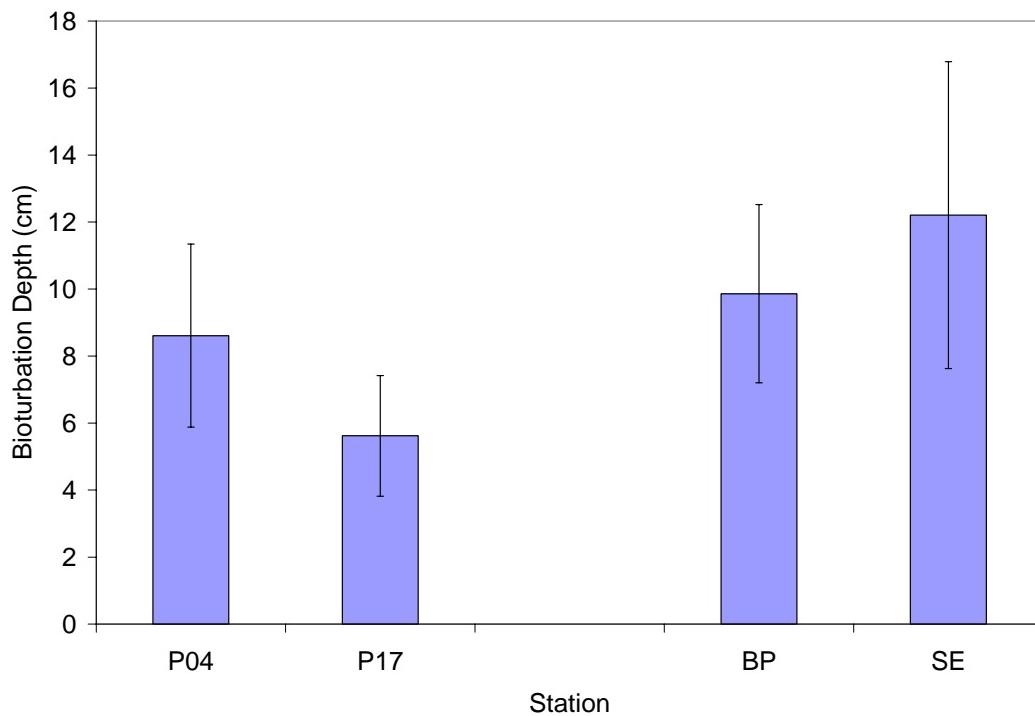


Figure 2-1. Comparison of biological mixing depths between Paleta Creek (P04, P17), and Pearl Harbor (BP, SE) sites.

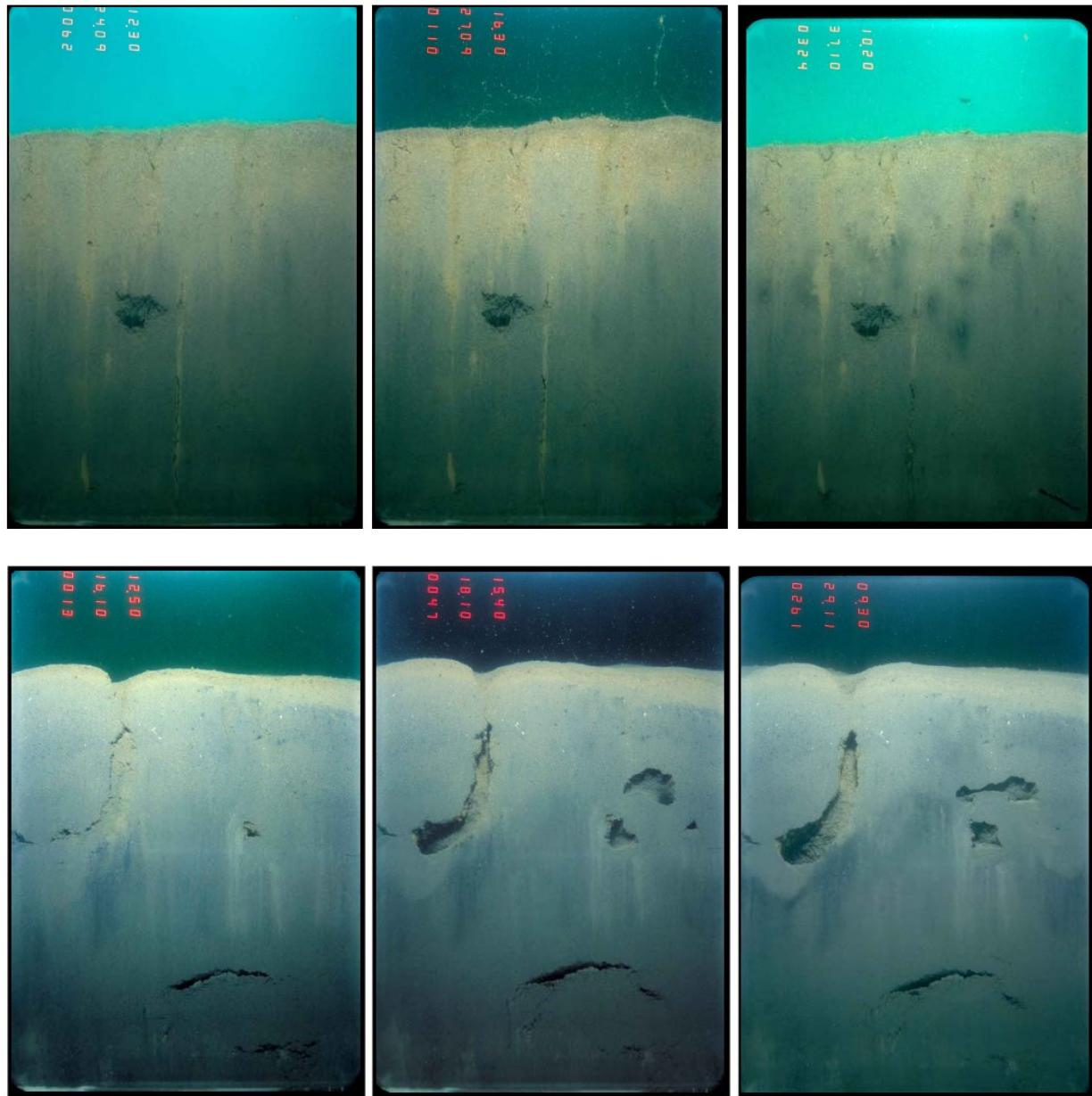


Figure 2-2. Top panel: Sediment profile images from the start, middle, and end of the time lapse deployment at Bishop Point Station C. Bottom panel: Sediment profile images from the start, middle, and end of the time lapse deployment at SE Loch Station B (Scale: Width of images = 15 cm).

## 2.3 ADVECTIVE FLUX

Advective flux rates were calculated based on two measurement data sets. Specific discharge rates ( $w$ ) were determined from multiple deployments of ultrasonic seepage meters within each site. Porewater concentrations were measured in the laboratory from composite samples collected at the same stations where the seepage meters were deployed. Porewater concentrations were determined for the sediments in the mixed layer ( $c_H$ ), and the overlying surface water ( $c_O$ ). For the Paleta Creek sites, concentrations below the mixed layer ( $c_{H-}$ ) were assumed to be zero for metals (due to reduced conditions), or calculated based upon a partitioning ratio with the solid concentration for PAHs. For the Pearl Harbor sites, concentrations below the mixed layer were measured directly from the core samples. The advective flux for a given chemical was then estimated as

$$F_A = \begin{cases} w(c_{H-} - c_H) & w \geq 0 \\ F_A = w(c_H - c_O) & w < 0 \end{cases} \quad (1)$$

Advective fluxes were calculated for each station at each site based on the equations above. The magnitude, direction and uncertainty of the advective flux depends upon the magnitude, sign and uncertainty of the specific discharge rates, and of the porewater and/or porewater/seawater gradients.

At Paleta Creek, Site P04, specific discharge rates were always positive (out of the sediment), ranging from a low of about 4 cm/d to a high of about 11 cm/d. Highest discharge developed during and following the lower low tide. Decreased levels of discharge corresponded to the period extending from the lower high tide, through the higher high tide. At station P17, specific discharge rates were always positive at the inner station (P17-3a), ranging from a low of about 3 cm/d to a high of about 8 cm/d. Highest discharge at the inner site generally occurred during both the higher and lower low tide conditions. At the outer site (P17-3b), seepage rates were generally positive, but there were some periods of slight negative flow (recharge). Seepage rates at the outer site ranged from about -0.5 to 6 cm/d. Along with the magnitude, the pattern of flow at the outer site was somewhat different than at the inner site. At the outer site, highest discharge generally occurred in association with the ebb tide prior to lower low water, not during both low water conditions. Variability at these stations appeared to be largely controlled by tidal action. This is also consistent with previous observations of seepage in tidally influenced coastal environments. Most results suggest a damping of discharge during the higher low tide, with strongest discharge occurring during the lower low tide. At both stations, the tidal variability represented about 30% of the overall signal.

In Pearl Harbor, variability in the specific discharge time-series at each station was influenced by tidal and upland variations in hydraulic gradients, as well as potential variations in biological irrigation. For Bishop Point, variations associated with tidal forcing appeared to be fairly weak at all stations, with typical ranges of 2-3 cm/day. Some short-term variability was observed at BPA and BPC that may have been related to bioirrigation. At Southeast Loch, tidal variations of 2-3 cm/day were also observed in the specific discharge, and bioirrigation appeared to be strong at SLB with fluctuations of 5-6 cm/day.

Measured seepage rates were used to determine tidally-averaged specific discharge rates at both sites (Table 2-2). Tidally-averaged specific discharge rates across the two sites were comparable, and the variation among replicates was also comparable, even though the spatial separation at the Pearl Harbor stations was significantly greater than for Paleta Creek. Typical replicate RSDs for specific discharge were on the order of 100% with a range from about 80-140%, thus spatial heterogeneity of discharge rates makes a significant contribution to the overall variability in the measurement of advective contaminant flux.

Porewater and surface water COPC concentrations are the other primary input to the advective flux field measurement estimates. Cross-site comparative porewater and surface water concentrations are shown for selected metals in Figure 2-3, and for selected PAHs in Figure 2-4. Note that for the Paleta Creek stations, values for  $c_{H^-}$  were inferred (no direct measurements), while for Pearl Harbor stations direct measurements were made. High-resolution cores and microprofiles indicated anoxic conditions with presence of sulfide in the deeper portion of the sediment column. Based on these observations, it was inferred that porewater metal concentrations would approach zero due to binding and formation of insoluble metal-sulfides. For PAHs, deep porewater concentrations at the Paleta site were inferred from solid phase concentrations based on the assumption that the PAHs would partition in the same proportion as observed in the surface sediment layer ( $c_H$ ).

In general, porewater and surface water metal concentrations for the two sites were of similar magnitude, but showed differing trends for different COPCs. For Arsenic, comparison of the two sites indicated very similar trends, with low surface water, and relatively higher mixed layer and deep layer concentrations. In contrast to the cross-site similarity for Arsenic, zinc profiles for the two sites were significantly different, with relatively low surface water concentrations at the Pearl Harbor stations, and relatively low mixed layer concentrations at the Paleta Creek stations. Since all sites had positive mean seepage rates, the contaminant advection is determined by the second equation above, which depends on the subsurface porewater gradient between H and  $H^-$ . For this reason, it is important to note that the assumption for Paleta Creek stations of  $c_{H^-} \sim 0$  was not borne out from the Pearl Harbor direct measurement results. It can be seen that the metals measured in porewaters extracted from composited cores below the mixed layer were not zero, but have measurable values, often comparable to or higher than those in the mixed layer. It is difficult to say whether these values, however, are more “correct” than the inferred values, because it is possible that metals were mobilized into the extracted porewaters during sample handling, despite significant care to minimize exposure. However, it seems clear that the refinement between Sites 1 and 2 of collecting and analyzing porewaters from below the mixed layer is a more appropriate approach than is assuming zero. Based on inferred concentrations, it is likely that the Paleta Creek estimates of metal advective fluxes are overestimates, since they most likely overestimate the subsurface metal gradients. Spatial replicate RSDs for porewater and surface water metals ranged from about 2-130%, with typical values ~30%. Thus spatial variations in porewater metals within stations/strata appears to contribute less to the overall variability of the advective metal flux estimate than the variations in seepage rates.

In contrast to metals, porewater and surface water PAH concentrations were significantly different across the two sites, with much higher concentrations at the Pearl Harbor stations

relative to the Paleta Creek stations. In general, mixed layer and deep layer porewater concentrations exceeded surface water concentrations at both sites. However, the gradients were significantly higher at the Pearl Harbor stations. Since all sites had positive mean seepage rates, the contaminant advection was determined by the second equation above, which depends on the subsurface porewater gradient between H and H-. Subsurface gradients were different for different PAHs and for different stations. For example, Naphthalene generally had lower concentrations in the deep layer at all stations, while other PAHs had significantly higher concentrations in the deep layer at Southeast Loch in Pearl Harbor. As with the metals, it seems clear that the refinement between Sites 1 and 2 of collecting and analyzing porewaters from below the mixed layer is a more appropriate approach for estimating the advective flux, however the partitioning approach used for the PAHs probably provides more realistic estimates than the zero concentration assumption used for metals. Spatial replicate RSDs for porewater and surface water metals ranged from about 1-170%, with typical values ~60%. Thus spatial variations in porewater PAHs within stations/strata appears to contribute nearly as much as the variation in seepage rates to the overall variability of the advective PAH flux estimate.

Comparisons of the resulting advective fluxes are shown in Figure 2-5 for metals, and in Figure 2-6 for PAHs. In general, metals displayed a range of fluxes with lowest flux rates observed for Ag, Cd, and Pb. Moderate fluxes were observed for As, Cu, and Ni, and highest fluxes were consistently found for Zn. General agreement between the two sites was observed for the approximate magnitude and direction of fluxes for As, Cu and Zn. Clear differences were observed for Ni and Pb. These differences appear to hinge on the assumption of low metal concentrations in the deep sediment layer at the Paleta Creek stations. As mentioned previously, this assumption leads to a potential overestimate of the advective flux for metals at those stations. Thus these results must be viewed with caution. For PAHs, strikingly higher advective fluxes were estimated from the data at Pearl Harbor relative to Paleta Creek. The contrast between the stations is also interesting, with advection leading to positive fluxes (mass loss) at Bishop Point, as opposed to Southeast Loch where high PAH concentrations measured in the deep sediment suggest that advection could be acting as an ongoing source to the surface mixed layer. The variations in seepage rates and porewater chemistry led to within-station RSDs ranging from about 50-200% for most advective chemical fluxes.

When the two demonstration sites are compared, the effect of different approaches to defining dissolved metal levels below the mixed layer (assumed to be zero at Paleta Creek and measured in composited cores at Pearl Harbor) may be dominating the differences. For most metals, the stronger gradients between the mixed layer and below (whether real or not) and the higher and consistently positive advective flows result in higher, and consistently positive fluxes at Paleta Creek. Variability at the Paleta stations is generally lower than at the Pearl Harbor sites. In part, this is due to the lower variability in advective flow rates, but lower variability also results from the more consistent porewater values (and the lack of error propagated from an assumption of zero for porewater levels below the mixed layer). In the Pearl Harbor strata, smaller porewater gradients, and in many cases increases in mean metals concentrations with depth, highly variable porewater values, and the lower but more variable (and sometimes negative) advective flow rates result in lower, much more variable and sometimes negative advective flux rates for these metals at specific stations. For Ni, on the other hand, the high negative gradient and high variability makes Ni fluxes higher in magnitude, but highly variable, in the Pearl Harbor sites.

This raises an interesting question of how data are processed when substratum results are integrated into the flux equations. At Paleta Creek, with the smaller number of successful seep measurements and the assumed, rather than measured, porewater values for the deeper sediment layer, advective fluxes were calculated using the mean parameters (seep rates and porewater gradients) for the three substrata. At Pearl Harbor, with more substratum-specific data, the advective flux rates were calculated for each substratum, and these substratum-specific values were averaged for the mean. Figure 2-7 illustrates how these different approaches affect the mean and standard deviation for metal advective flux rates at the Pearl Harbor sites. As can be seen, although there are some differences in the ranges of results, there are no significant or consistent differences in the ranges, directions or variability of results.

Table 2-2. Comparison of tidally-averaged specific discharge rates for the PRISM stations in Paleta Creek and Pearl Harbor.

Site	Station	Seepage (cm/d)	Notes
Paleta Creek	P04	8.1±n/a	No replicate
	P17	3.5±3.1	Replicate seperation ~ 5 m
Pearl Harbor	BP	3.1±4.3	Replicate seperation ~ 25-50 m
	SL	4.0±3.1	Replicate seperation ~ 100-200 m

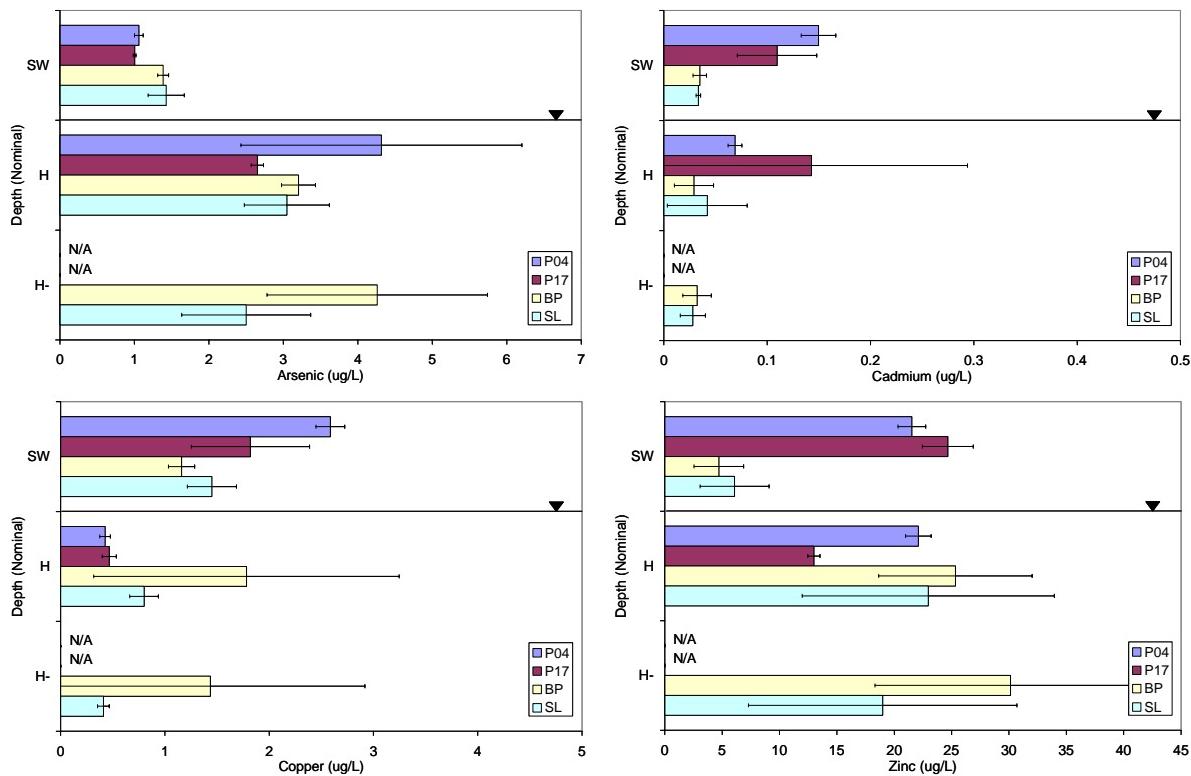


Figure 2-3. Representative metal surface water and porewater profiles for As, Cd, Cu and Zn.

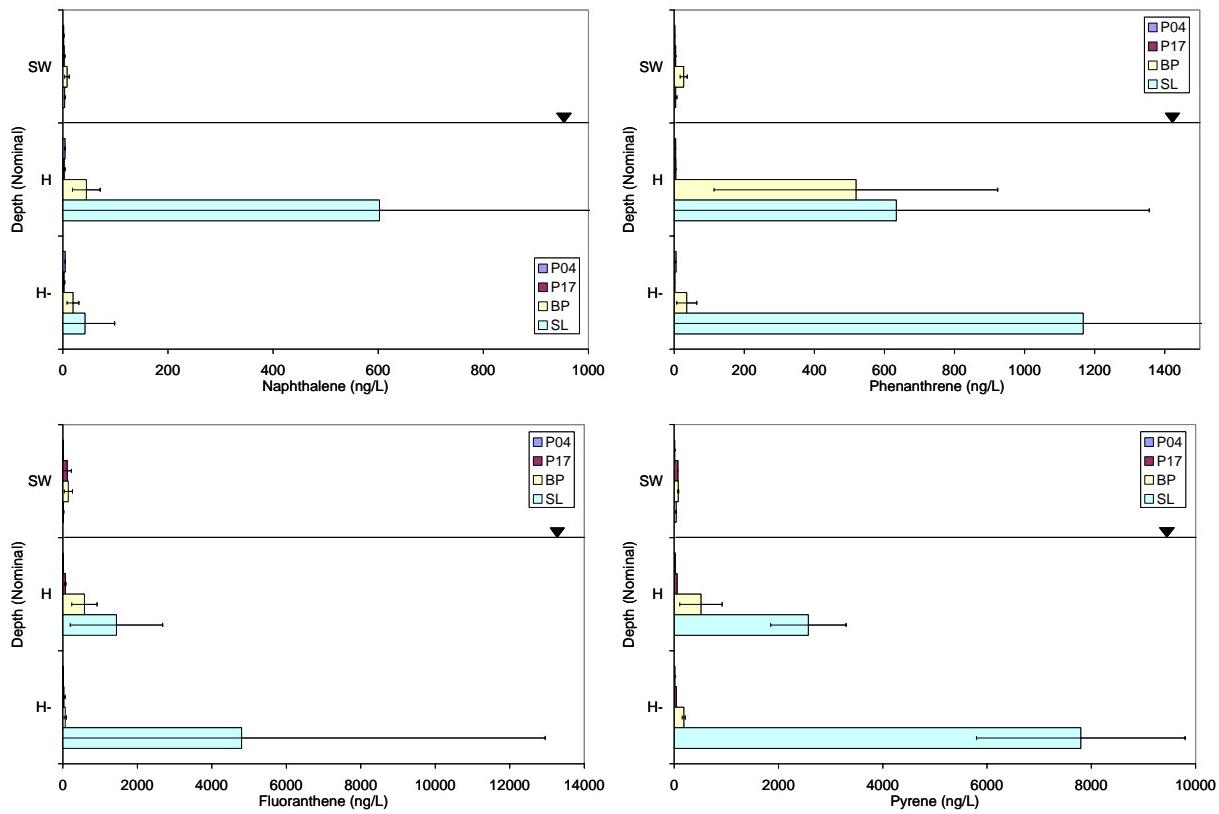


Figure 2-4. Representative PAH surface water and porewater profiles for Naphthalene, Phenanthrene, Fluoranthene, and Pyrene.

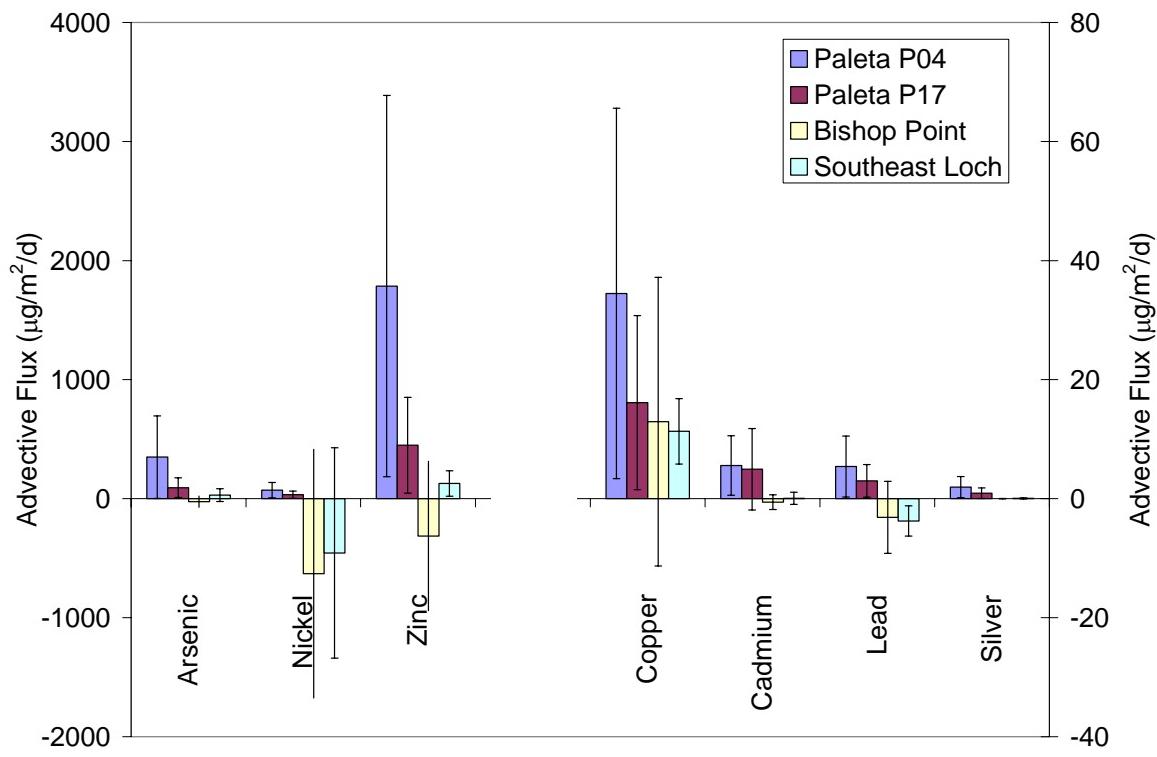


Figure 2-5. Cross-site comparison of advective metal fluxes. Note scale change for different groupings of metals on the left vs. the right. Positive fluxes indicate export from the surface sediment mixed layer.

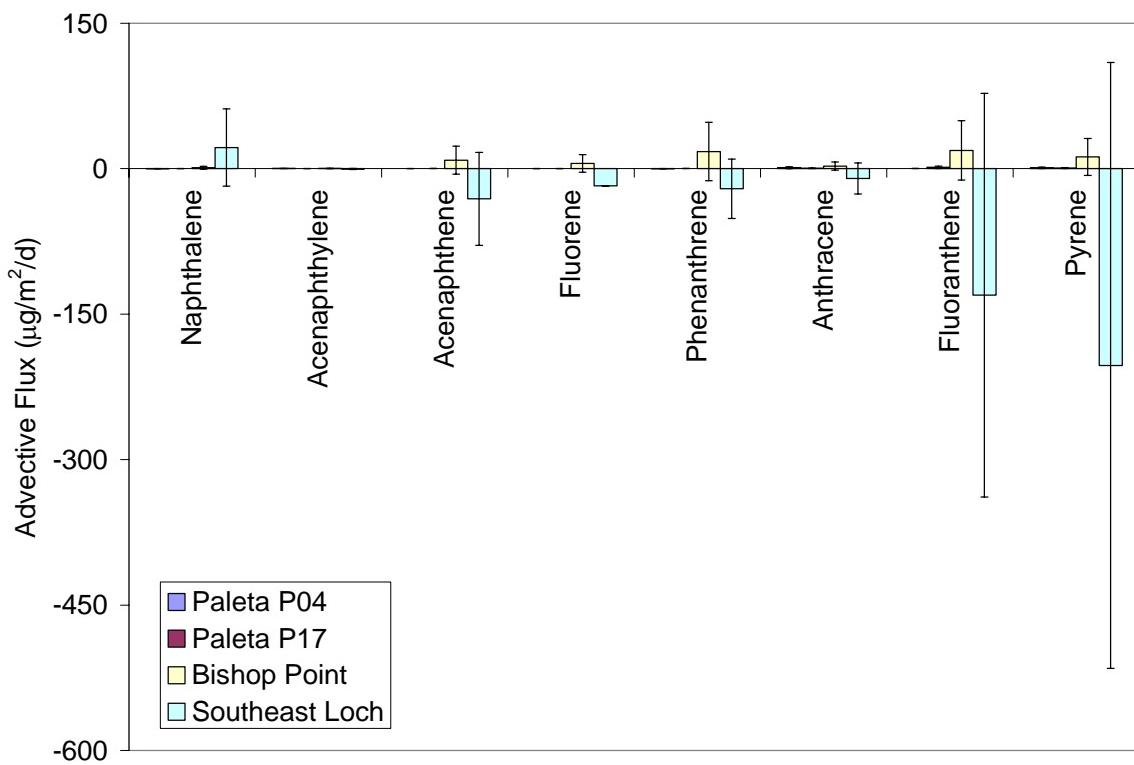


Figure 2-6. Cross-site comparison of advective PAH fluxes. Positive fluxes indicate export from the surface sediment mixed layer.

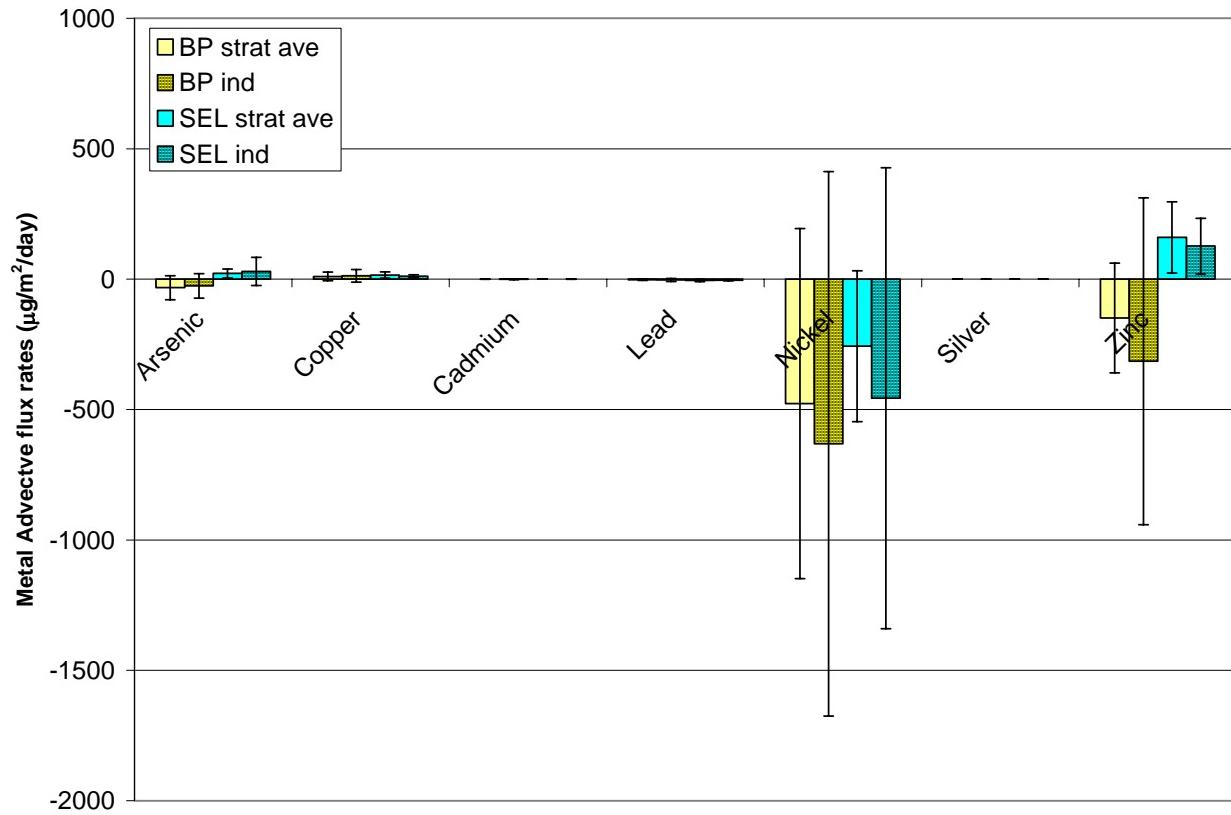


Figure 2-7. Comparison of Pearl Harbor advective fluxes calculated with substratum-averaged data (strata ave) and using the data from individual replicates within the substratum, and then averaging (ind). Positive fluxes indicate export from the surface sediment mixed layer.

## 2.4 DIFFUSIVE/BIOIRRIGATION FLUX

Fluxes associated with molecular and biologically mediated diffusive pathways were calculated directly from the time-series concentrations measured in the BFSD. Attempts to separate the biological component of the flux by limiting oxygen supply to the BFSD chamber were unsuccessful. Thus the reported flux rates represent the combined effect of all diffusive and bioirrigation processes. Because there is no flow path for water through the BFSD, the fluxes do not include advection. The diffusive flux was calculated from the time series data as

$$F_D = F_{DC} + F_{DB} = \frac{V}{A} \frac{dc}{dt} \quad (2)$$

Here V is the chamber volume, and A is the surface area of the sediment enclosed by the chamber. Diffusive fluxes were calculated for each replicate at each station/strata based on the equation above. The station/strata-mean flux was then calculated as the average of the replicate flux measurements. An important underlying assumption in this formulation is that there is no significant diffusive flux between the surface mixed layer and the deep layer.

Cross-site comparative results for metals are shown in Figure 2-8 and for PAHs are shown in Figure 2-9. In general, we found that fluxes for the target metal and PAH constituents were detectable in the majority of the deployments. In general, contaminant metals displayed a range of fluxes. Lowest flux rates were generally observed for Ag, Cd, and Pb. Moderate fluxes were observed for As, Cu, and Ni, and highest fluxes were consistently found for Zn. Cross-site comparison of metal fluxes for the two sites indicates highest Ni and Pb fluxes at Pearl Harbor stations, highest Cu and Zn fluxes at Paleta Creek, and fairly comparable fluxes of other metals. Mean flux rates for most metals at both sites were positive, indicating a general trend of release of metal from the sediment to the water column by this pathway. These patterns are consistent with previous BFSD results from a number of harbors that also showed lowest (based on means) flux rates for Ag, Cd, and Pb and highest fluxes for Zn. The range of metal flux rates measured in this study is also consistent with the larger historical data set, suggesting that the measurements obtained by this program should provide rates that are consistent with general trends observed across a number of harbors.

In general, PAHs displayed a range of fluxes with lower flux rates generally observed for Acenaphthene, Fluorene, and Phenanthrene. Higher fluxes were generally observed for Naphthalene, Acenaphthylene, Anthracene, Fluoranthene, and Pyrene. Cross-site comparison for the two sites indicates generally similar patterns of diffusive PAH fluxes, with some differences in magnitude, and particularly highest Fluoranthene and Pyrene fluxes at Pearl Harbor.

Variability in metal and PAH fluxes was observed on several distinct scales in this study including variability for a given measurement, replicate variability within a station (Paleta Creek; scale 2-10 m), replicate variability within a strata (Pearl Harbor; 25-200 m), variability between stations and strata (scale 1-5 km), and variability between the two demonstration sites.

Variability within an individual flux measurement is quantified based on the variance of the slope of the concentration with time. The variability in the slope may arise from a number of factors including actual non-linearity of the measured process, sample contamination, and analytical variability. For the BFSD, assessment of this variability is evaluated based on comparison to blank chamber runs (runs with a Teflon panel in place of sediment). Based on a

statistical comparison of the deployment data versus the blank, an assessment is made as to whether the flux is “detectable”. This simply means that a flux was detected by the instrument that can be distinguished from a flux when no sediment is present. This does not necessarily imply that the flux is significant from a transport or ecological perspective. By the same token, failure to detect a flux that is distinguished from the blank does not necessarily mean that the flux is insignificant, rather that with the BFSD technology, we are simply not able to determine a flux rate that is quantifiable in comparison to the blank. This is parallel to, for example, the measurement of a water concentration. If the concentration is detectable, we can quantify the value, but this does not infer that it exceeds an effects threshold. Similarly if we cannot detect it, but the effects threshold is below our detection limit, we cannot rule out a potential effect. For this reason, it is important to know whether fluxes were detectable when interpreting the data here, but we continue to use the entire data set for the general analysis so that perspective can be gained on the relative importance of fluxes within the context of PRISM.

Within station/strata variability was evaluated on the basis of three replicate deployments at each station/strata. In general, these results indicate a fairly high degree of variability. This is expected to some degree because of the heterogeneous nature of the sediments and the geochemical and biological processes that regulate fluxes. While the variability is not surprising, it is critical that it be quantified within the context of PRISM. Since the flux rates will be used to compare the relative importance of various processes within a general transport balance, quantification of within site variability will allow the range of possible outcomes to be explored. Comparison of variability within the stations at Paleta Creek vs. the strata approach used at Pearl Harbor indicate generally higher variability for PAH fluxes associated with the larger spatial separation at the Pearl Harbor strata. Variability for metals appeared to be fairly comparable for strata vs. station replicates. Replicate variability within stations/strata suggests that differences across stations, strata and demonstration sites is difficult to distinguish for some constituents, while clear differences are apparent for others. For example, despite significant replicate variability, fluxes of zinc at Paleta P17 are clearly higher than those observed at Pearl Harbor. Similarly, Pyrene fluxes at Bishop Point are clearly higher than those observed at Paleta Creek.

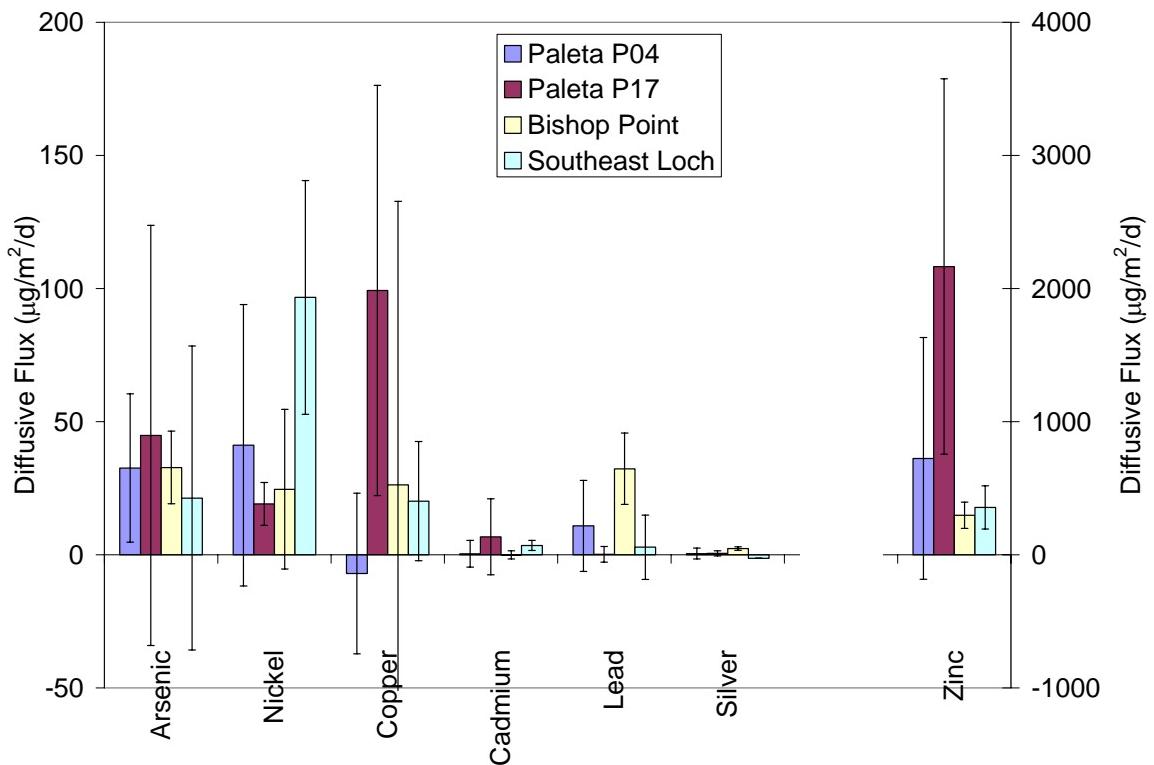


Figure 2-8. Cross-site comparison of diffusive metal fluxes. Note scale change for different groupings of metals on the left vs. the right. Positive fluxes indicate export from the surface sediment mixed layer.

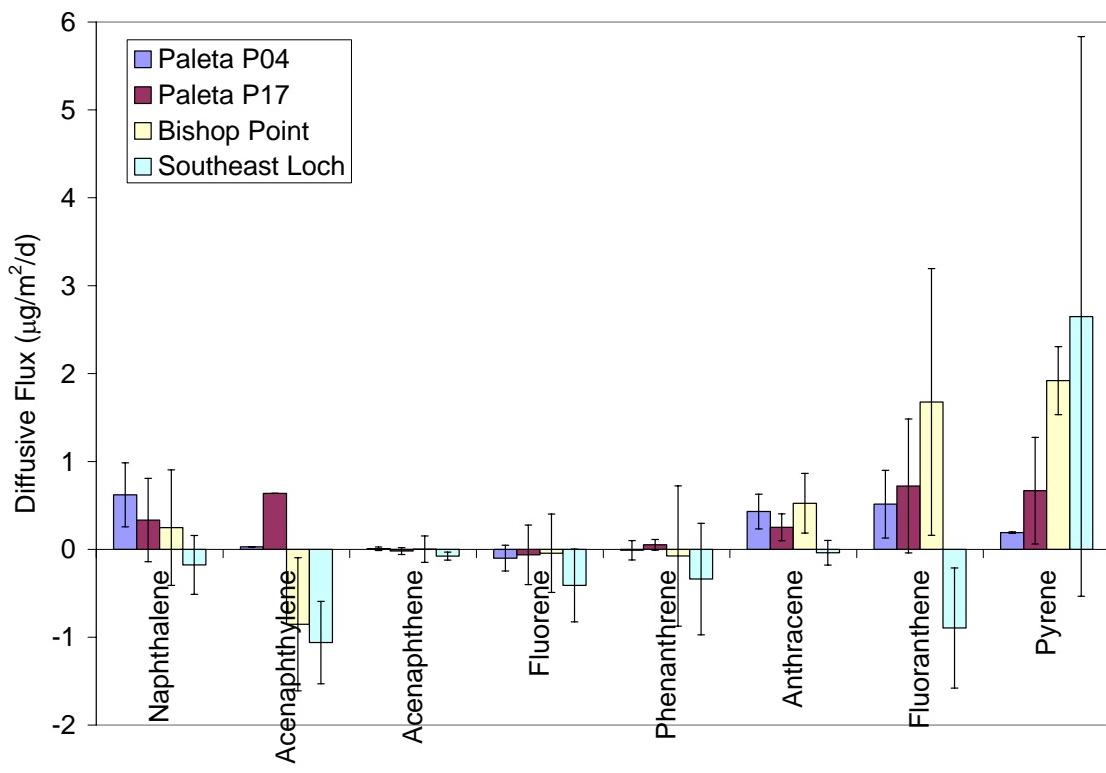


Figure 2-9. Cross-site comparison of diffusive PAH fluxes. Positive fluxes indicate export from the surface sediment mixed layer.

## 2.5 FLUX BY SEDIMENTATION

For the Paleta Creek stations in this study, two mechanisms of sedimentation flux were considered, and they were calculated differently. Sedimentation was considered to have two components; a constant “background” sedimentation and an occasional storm-induced sedimentation. “Background” sedimentation rates were based upon trap sedimentation rates. For P17, since age-dated core rates were significantly higher than trap rates, storm-induced sedimentation rates were derived from a study at Paleta Creek, which evaluated the volume (and COPC levels) of particles that were deposited into Paleta Creek during storms (Katz et al., in prep.). For P04, which is further from the creek mouth, trap rates are higher than age-dated core rates, and thus the storm input is considered to be negligible. Sedimentation rates determined by age dating were found to be unreliable for Southeast Loch due to perturbation of the historical record by recent dredging activities. Thus, to be consistent, trap measurements were used for both Pearl Harbor sites. For Pearl Harbor, insufficient data was available to evaluate storm inputs, and the stations were generally remote from any significant stream discharges, so storm sources were neglected. For cross-site comparative purposes, only estimates of the total sedimentation flux are discussed here.

Fluxes associated with sedimentation were calculated from trap and storm study derived sedimentation rates ( $S_t$  and  $S_s$ ), and trap ( $c_S$ ), bed ( $c_B$ ), and storm particle ( $c_{ss}$ ) contaminant concentrations. When new sediment deposits on the bed, the contaminant load of the mixed layer can be changed in several ways. If the depositing sediment is cleaner than the bed, then the sedimentation will reduce the concentration in the mixed layer. Alternatively, if the depositing sediment is more contaminated than the bed, then the sedimentation will increase the concentration in the mixed layer.

The background sedimentation flux was calculated from the sediment trap data as

$$F_{sB} = S_t(c_B - c_S) \quad (3)$$

and the storm-induced sedimentation flux was calculated as:

$$F_{sS} = S_s(c_{ss} - c_S) \quad (4)$$

Background sedimentation fluxes were calculated for each station at each site based on the equations above. The site-mean fluxes were then calculated as the average of the stations fluxes within the site. Storm-induced sedimentation fluxes were based upon data in the Katz et al. study, and thus were not done for each station, but calculated once for P17. It should be noted that resuspension effects can lead to a high bias in sedimentation rates from trap. However, in the context of contaminant deposition, if the material is resuspended sediment, the deposition rate will be negligible because the depositing sediment and bed sediment concentrations will be approximately the same ( $c_S \approx c_B$ ).

As described above, the estimate of settling flux depends largely on the measurements of sedimentation rate and the difference between the concentration of COPCs in the settling material compared to the surface sediment. Sedimentation rates for the two demonstration sites

are shown in Figure 2-10. Rates were generally similar across sites, in the range of 1-2 cm/d. These rates are typical of coastal harbors and embayments. Estimates suggest that about half the sedimentation at the creek mouth station P17 is contributed by stormwater runoff events. Replicate measurements at the Paleta sites showed low variability (RSDs <10%), while the more widely separated stations in the Pearl Harbor strata had significantly higher variability (RSDs ~50-100%).

Cross-site comparison plots of trap sediment metals vs. surface sediment metals are shown in Figure 2-11. Trap sediments followed similar general patterns of concentration for the two demo sites with some notable exceptions such as Cu and Zn at Southeast Loch, and Cu, Zn and Cd at P17. For the surface sediments, metals were generally higher at the Pearl Harbor stations compared to Paleta Creek, particularly Cu and Zn. Replicate variability in trap and surface sediment concentrations was generally low (RSDs 10-20%), though somewhat higher for particular metals at particular stations (e.g. Ag at SL and Cu and Zn at BP). The settling flux is driven by the difference between these concentrations. Clear differences are evident for example at Paleta Creek where Cu and Zn in the traps always exceeded Cu and Zn in the surface sediments, and at Bishop Point where Cu and Zn in the traps was significantly lower than in the surface sediments. These differences suggest significantly different conditions are present at these sites that are relevant to understanding the potential risk and recovery.

Similar cross-site comparison plots of trap vs. surface sediment PAHs are shown in Figure 2-12. Trap and surface sediment PAHs followed similar general trends of concentration for the two demo sites with higher concentrations for higher molecular weight PAHs (e.g. Fluoranthene and Pyrene). PAHs were significantly higher in the Bishop Point traps, while trap concentrations at P17 and Southeast Loch were moderate and comparable, and P04 concentrations were consistently the lowest. For the surface sediments, PAHs were consistently higher at the Pearl Harbor stations compared to Paleta Creek. Replicate variability in trap and surface sediment concentrations of PAHs was generally lower in the Paleta Creek stations and higher and the more spatially distinct Pearl Harbor stations. The settling flux is driven by the difference between these concentrations. Clear differences are evident for example at Paleta Creek stations and Bishop Point where PAHs in the traps always exceeded PAHs in the surface sediments, and at Southeast Loch where PAHs in the traps were significantly lower than in the surface sediments. As with metals, these differences suggest significantly different conditions are present at these sites that are relevant to understanding the potential risk and recovery.

Results for settling fluxes of metals and PAHs are shown in Figure 2-13 and Figure 2-14, respectively. Among the metals, Cu, Pb and Zn generally had higher settling fluxes, and As, Cd, Ni and Ag had lower fluxes. Cross-site comparison indicates that settling fluxes at Paleta Creek were consistently negative (source to the surface layer) and of lower magnitude when compared to Pearl Harbor stations. Fluxes at the two stations in Paleta Creek were generally comparable, while fluxes in the two strata in Pearl Harbor were distinctive. For Southeast Loch, Cu and Zn settling added to the surface sediment mass, while As and Ni indicated loss of mass. In contrast, Bishop Point results indicated strong positive fluxes for most metals indicating a general reduction in surface sediment loading as a result of settling. For PAHs, settling fluxes at both sites for most PAHs indicated settling as a source to the surface layer, with the exception of the heavier molecular weight PAHs at Southeast Loch. Settling fluxes (whether positive or negative)

were generally of higher magnitude at Pearl Harbor, consistent with the stronger contaminant gradients observed in the traps and sediments.

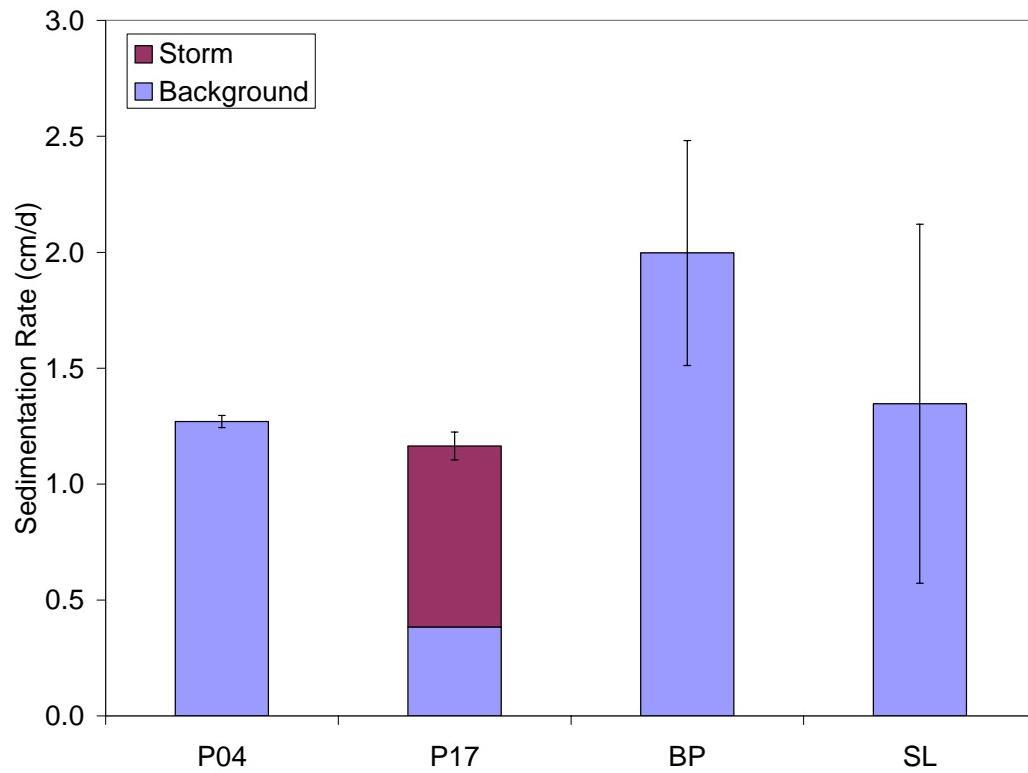


Figure 2-10. Cross-site comparison of sedimentation rates measured by replicate sediment traps at the two demonstration sites.

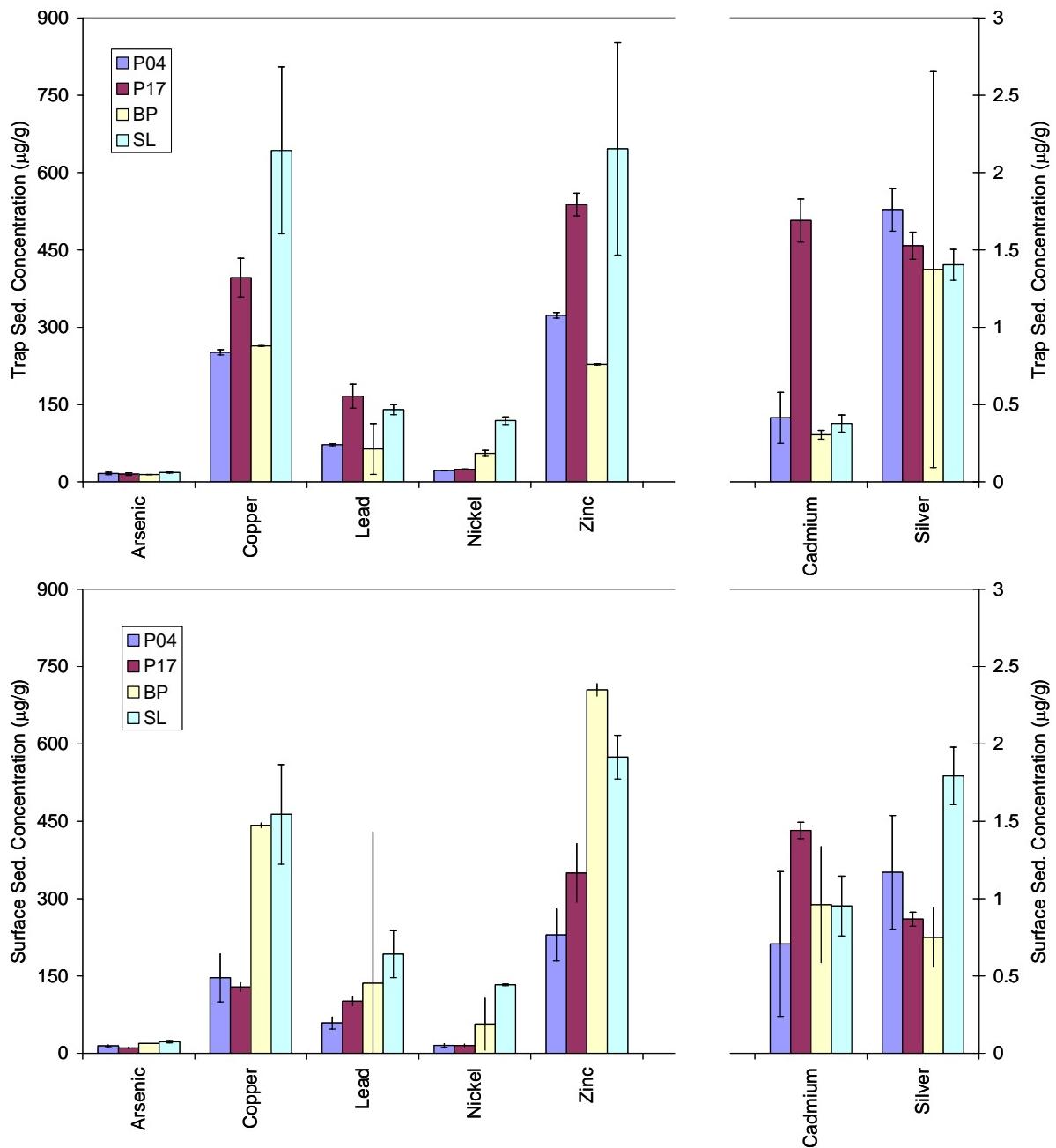
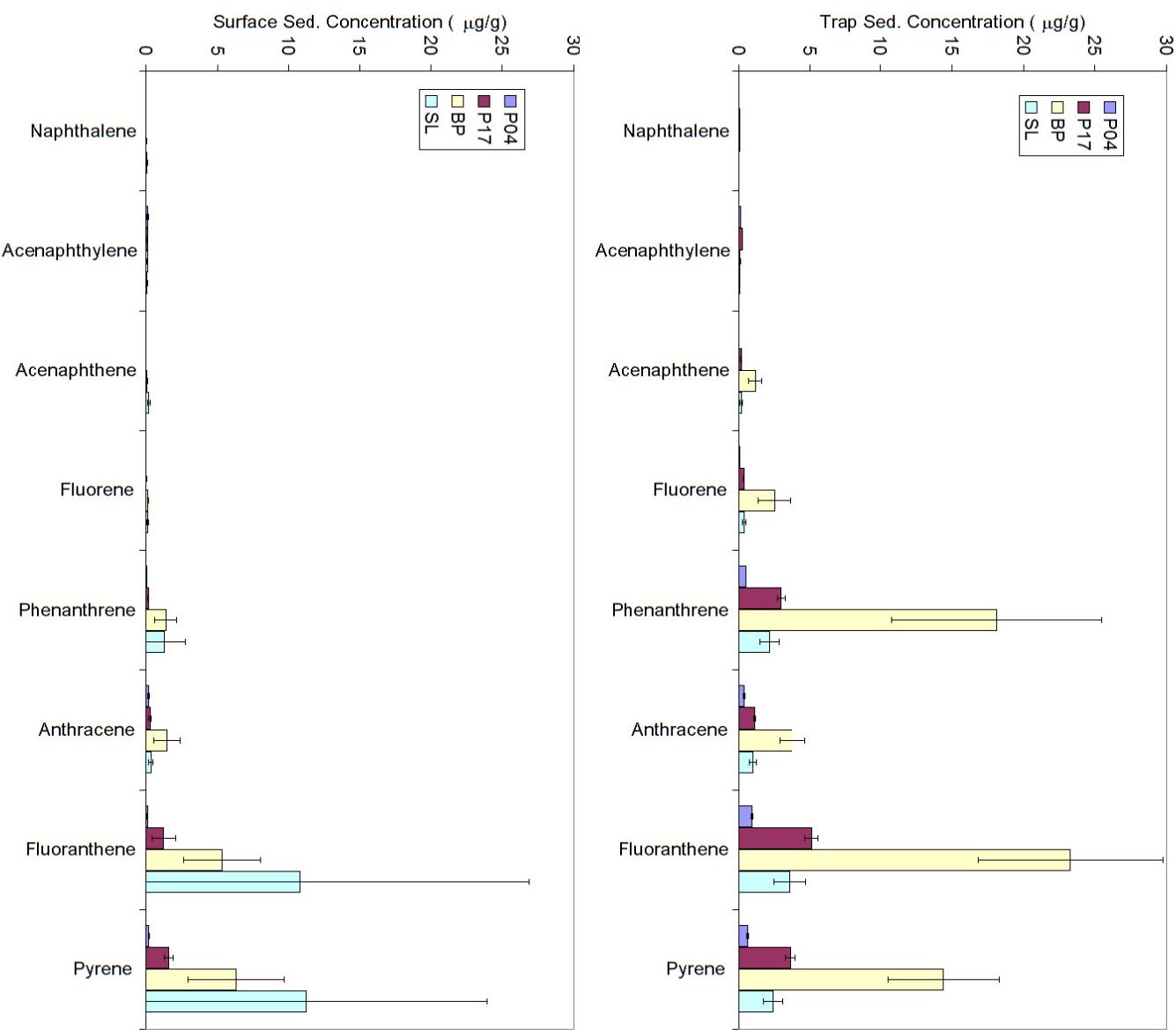


Figure 2-11. Cross-site comparison of trap (upper) and surface (lower) sediment metal concentrations. Note scale change for different groupings of metals on the left vs. the right.

Figure 2-12. Cross-site comparison of trap (upper) and surface (lower) sediment PAH concentrations.



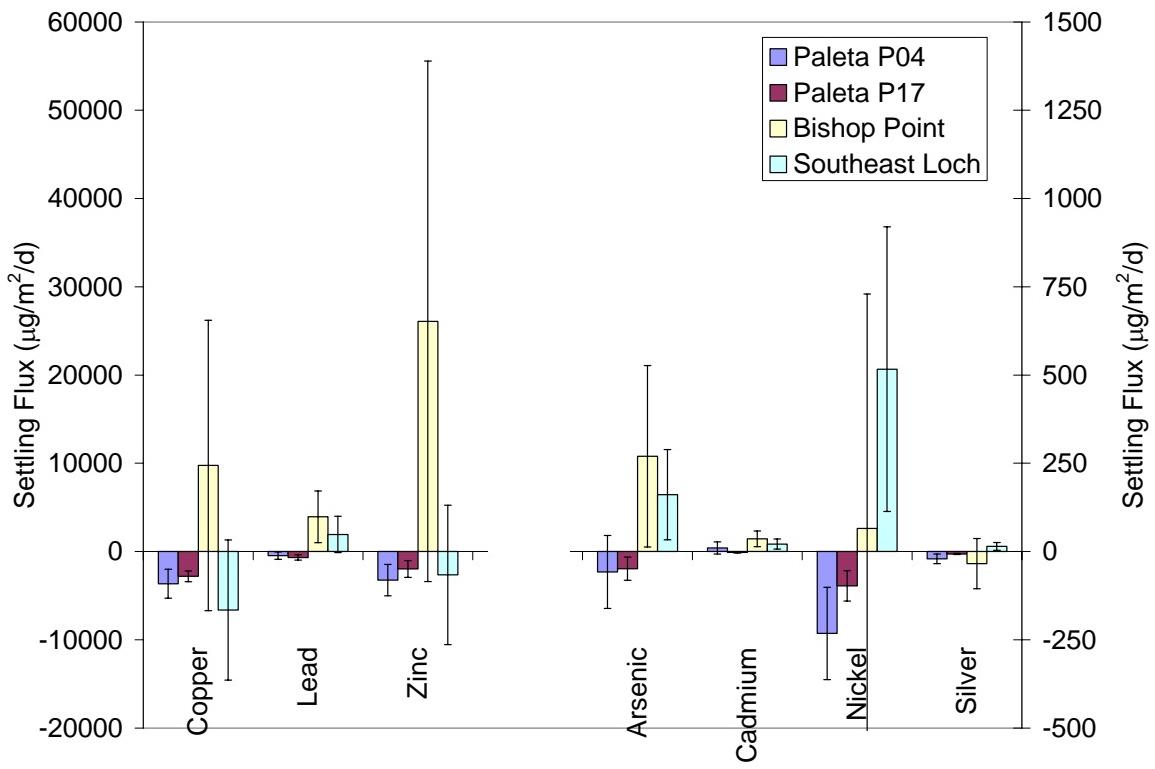


Figure 2-13. Cross-site comparison of settling fluxes for metals. Note scale change for different groupings of metals on the left vs. the right. Positive fluxes indicate export from the surface sediment mixed layer.

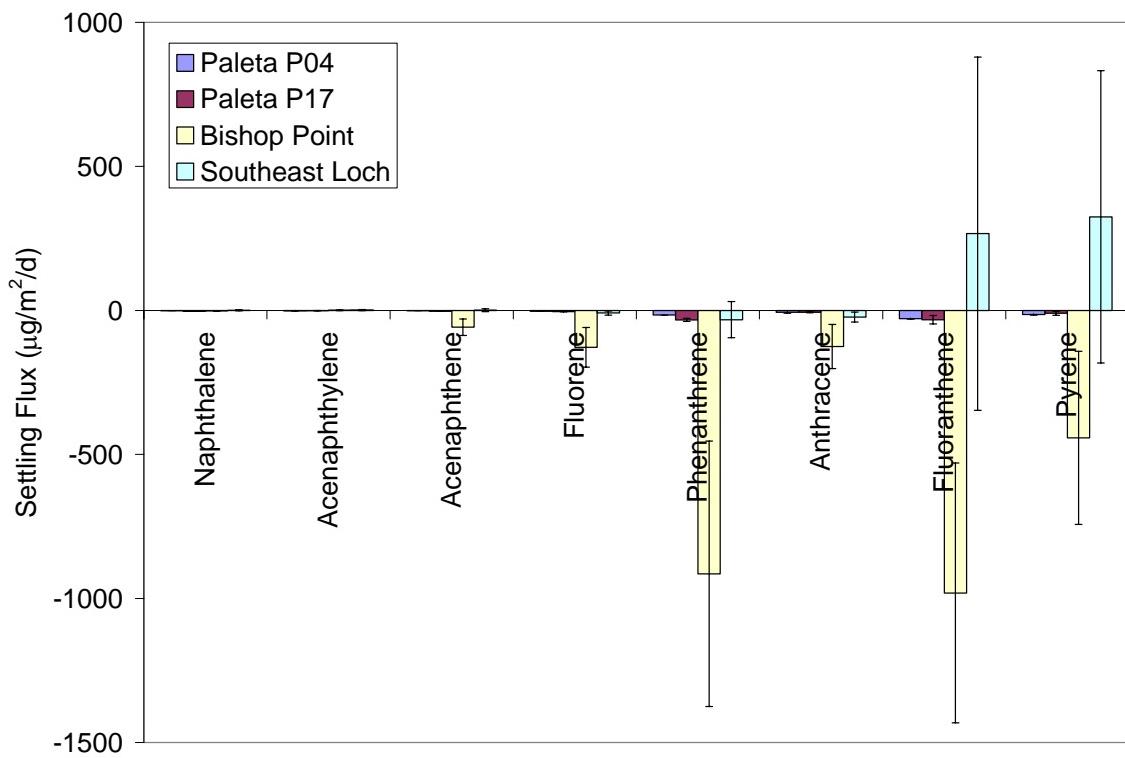


Figure 2-14. Cross-site comparison of settling fluxes for PAHs. Positive fluxes indicate export from the surface sediment mixed layer.

## 2.6 FLUX BY EROSION/RESUSPENSION

Fluxes associated with erosion were evaluated from critical shear stress ( $\tau_c$ ) and erosion rate ( $K_E$ ) characteristics measured by the flumes, bed shear stresses ( $\tau$ ) estimated from the current meters, and the contaminant concentrations measured within and below the mixed layer ( $c_{H-}$ ,  $c_H$ ). If the bed shear stress at the site exceeds the critical shear stress, then the potential exists for sediments to be eroded from the bed and transported by the harbor currents. In this case, the amount of erosion depends on the erosion rate characteristics of the bed as a function of depth, and the strength, variability, and duration (T) of the applied shear stress. The erosion flux was calculated from the sediment flume and current meter data as

$$F_E = \frac{c_H - c_{H-}}{T} \int_0^T K_E(z)(\tau(t) - \tau_c)dt \quad (5)$$

Variation in the erosion flux across sites thus depends on: variation in the current meter time-series record at each station; variation in critical shear stress and erosion rate coefficients determined by two different flume systems, the in-situ annular Sea Carousel, and the axial laboratory SedFlume; and variation in contaminant concentrations below and within the mixed layer between stations within the same site.

Within the accuracy of the measurement, the critical shear stress was found to be the same value, 0.17 Pa, in both replicates at both Paleta Creek sites. Critical shear stress at the Pearl Harbor stations was generally lower, and particularly for the Southeast Loch sediments where critical shear stress was about half the value observed at other locations (Figure 2-15). Erosion rate of consolidated fine sediments tends to vary down core as a function of the applied excess shear stress (excess over the critical shear; see Figure 2-16). Erosion rate characteristics were similar for the Paleta Creek stations and the Bishop Point station, but again departed from this trend at the Southeast Loch station. At the Southeast Loch station, smaller applied excess shear stress resulted in larger erosion rates, and the erosion rate increased less dramatically with higher applied excess shear. This is consistent with the strong biological reworking observed in these sediments by the SPI study. In general, these results suggest that, under similar applied stress conditions, sediments at Southeast Loch have a higher potential for erosion compared to other areas evaluated in this study.

Applied bed stress as estimated by near-bottom current meters was influenced primarily by tidal and wind driven forcing of water currents. In general, very low current speeds were observed at both demonstration sites. At the Paleta stations, some short-term, high-current events were observed. There were believed to be related to ship and tug movements in the area. Tidal variations in Pearl Harbor are smaller than many coastal sites, and this was particularly true for the Southeast Loch site, which is located at the head of the Loch and is thus subjected to a minimum of tidal through flow. Because of its location near the entrance channel to Pearl Harbor, the Bishop Point site is subject to higher tidal fluctuation in currents. Tidal fluctuations of near-bottom currents at the Southeast Loch site were generally <1 cm/s, while for Bishop Point, tidal fluctuations were generally <5 cm/s. These components appeared to be relatively

consistent during the measurement period, but may fluctuate seasonally depending on wind patterns and river flow.

Based on these current velocities, the calculated bottom shear at Paleta Creek stations was generally very low (SL & P17: ~0.1 dyn/cm<sup>2</sup>; BP & P04: 0.5-2 dyn/cm<sup>2</sup>) during the majority of the measurement conditions. During the suspected ship movement events at Paleta Creek, shear stresses at both sites exceeded 10 dyn/cm<sup>2</sup>. These higher energy events were not detected during the Pearl Harbor deployments, but it is likely they do occur. Comparison of these estimated shear stresses to the measured critical shear stress at the sites (0.17 Pa = 1.7 dyn/cm<sup>2</sup>) indicates that the critical shear stress at BP and SL was never exceeded, and the critical shear stress at P17 was only exceeded during high energy events such as ship movements. At P04 the results indicated that the critical shear stress was exceeded during high energy events, but was also exceeded slightly during peak tidal flows. Analysis of the high energy events indicates that they occur about 1-2 times per week, and persist for about 10-30 minutes. This is consistent with the frequency and duration of ship movements in the Naval Station (Paleta Creek) area. The net erosion rate for the Paleta Creek stations was about 2.0 g/m<sup>2</sup>/d for P04, and about 0.8 g/m<sup>2</sup>/d for P17.

Where erosion was predicted to occur, the flux of a contaminant depends on the concentration gradient between the mixed layer and the deep layer. If the concentration in the mixed layer (H) is lower than the concentration in the deep layer (H-), then as the surface layer erodes the concentration in the mixed layer will increase. Cross-site comparison of metal concentrations in the mixed and deep layers are shown in Figure 2-17. Metal concentrations in both layers were generally higher at the Pearl Harbor stations, with the exceptions of Cd and Ag. Vertical gradients varied across stations and sites, with generally higher concentrations in the deeper sediments at P04 and SL, minimal difference at BP (except Cu), and higher concentrations in the surface layer for P17, particularly for Cu and Zn. Cross-site comparison of representative PAH concentrations in the mixed and deep layers are shown in Figure 2-18. PAH concentrations in both layers were generally higher at the Pearl Harbor stations. Vertical gradients varied across stations and sites, with generally higher concentrations in the shallower sediments at P04, P17, and SL, and minimal difference at BP.

At both sites, the flux associated with erosion was at most times negligible, at least under the conditions represented by the current meter deployments, except during ship movements. Estimated erosion fluxes are shown in Figure 2-19 for metals, and in Figure 2-20 for PAHs. The upper panel in each figure shows the estimated fluxes using the applied shear stresses calculated from the current meters at each station. For this result, the Pearl Harbor fluxes are zero, because the applied shear never exceeded the critical shear. In the lower panel, fluxes are shown assuming the that net erosion rate at Pearl stations is comparable to that at Paleta Creek. This provides a means of gaging the potential for erosion based on the assumption that higher energy event occur at Pearl at the same frequency as Paleta, but were not captured in the limited measurement record.

The results indicate that at P04, the concentration of several metals (Cu, Pb, Ni, Zn) increase as the mixed layer erodes as a result of higher concentration of metals in the deep layer. At P17 the opposite occurs, particularly for Cu and Zn. Potential for erosive fluxes at the Pearl sites based on the Paleta erosion rates indicate that erosion could result in significant mass loss of metals

from the surface sediments at BP, particularly for Cu and Zn. This should be viewed as an erosion potential, since as previously mentioned, the measured shear stress never exceeded the critical shear. For PAHs, the erosion flux at Paleta Creek stations generally resulted in a decrease in the mixed layer concentration. Potential for erosive fluxes at the Pearl sites based on the Paleta erosion rates indicate that erosion could result in significant mass loss of PAHs from the surface sediments at BP, and particularly for SL.

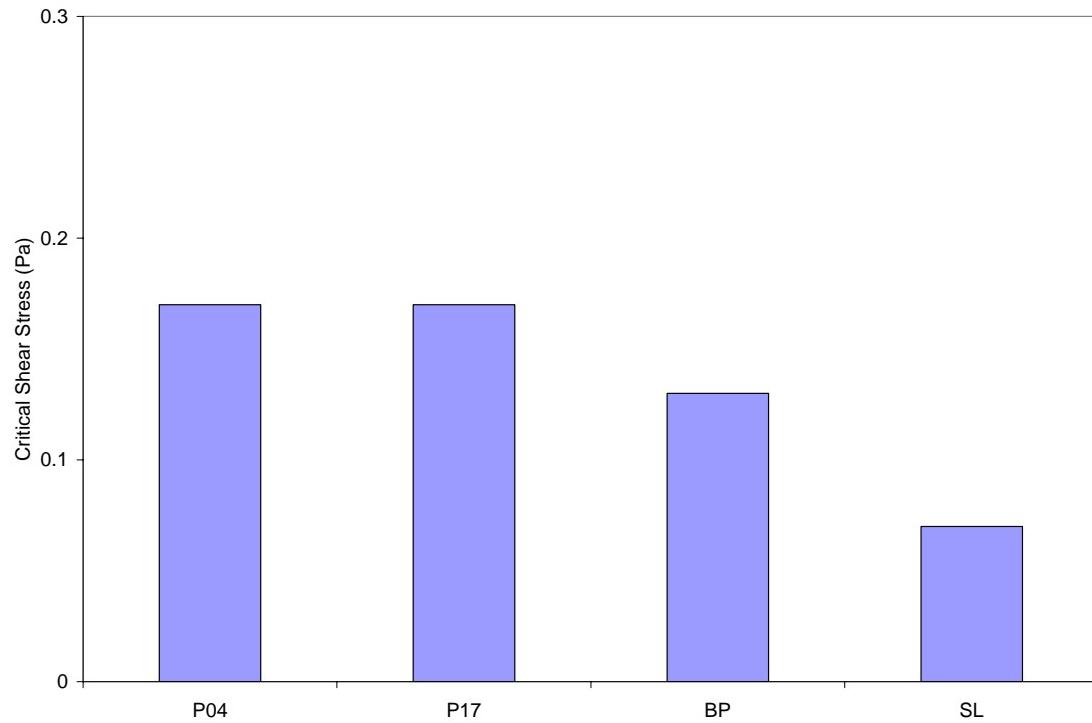


Figure 2-15. Cross-site comparison of critical shear stress measured in the Sea Carousel Flume. Replicate measures at the Paleta Creek stations were identical, and there were only single measurements at the Pearl Harbor stations.

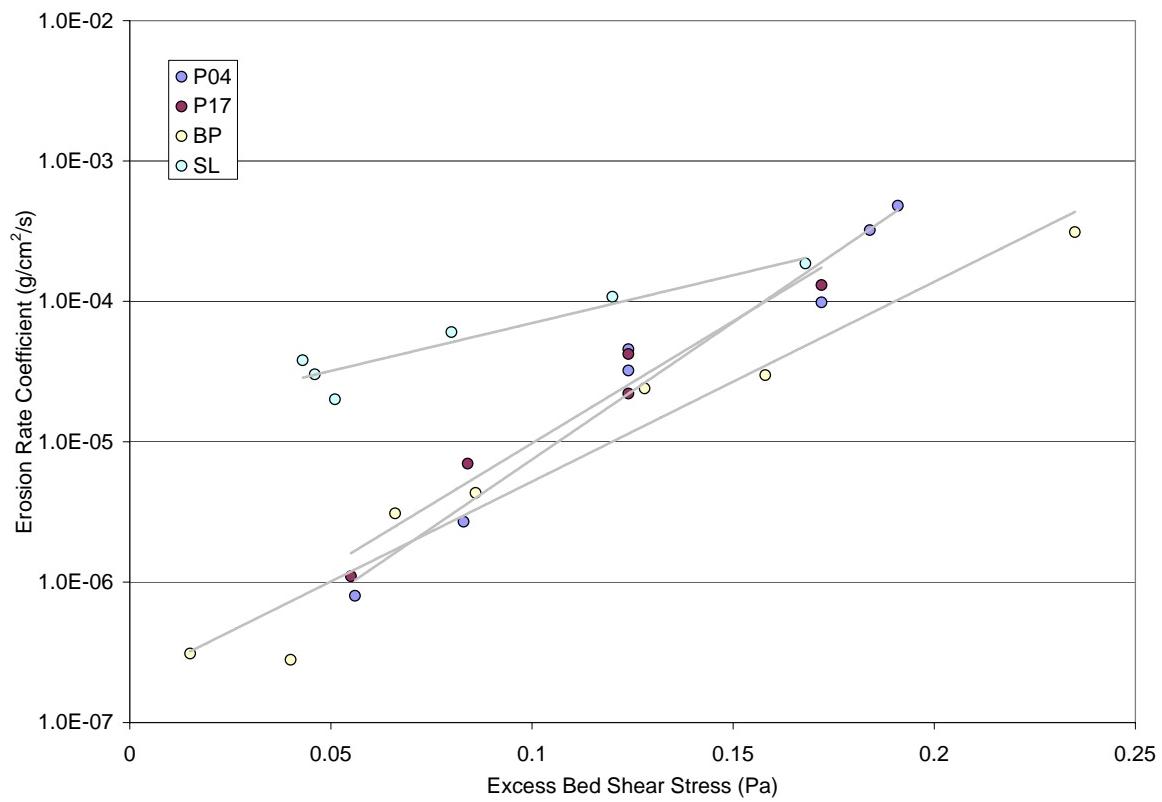


Figure 2-16. Cross-site comparison of the erosion rate coefficient as a function of excess bed shear stress as measured in the Sea Carousel Flume.

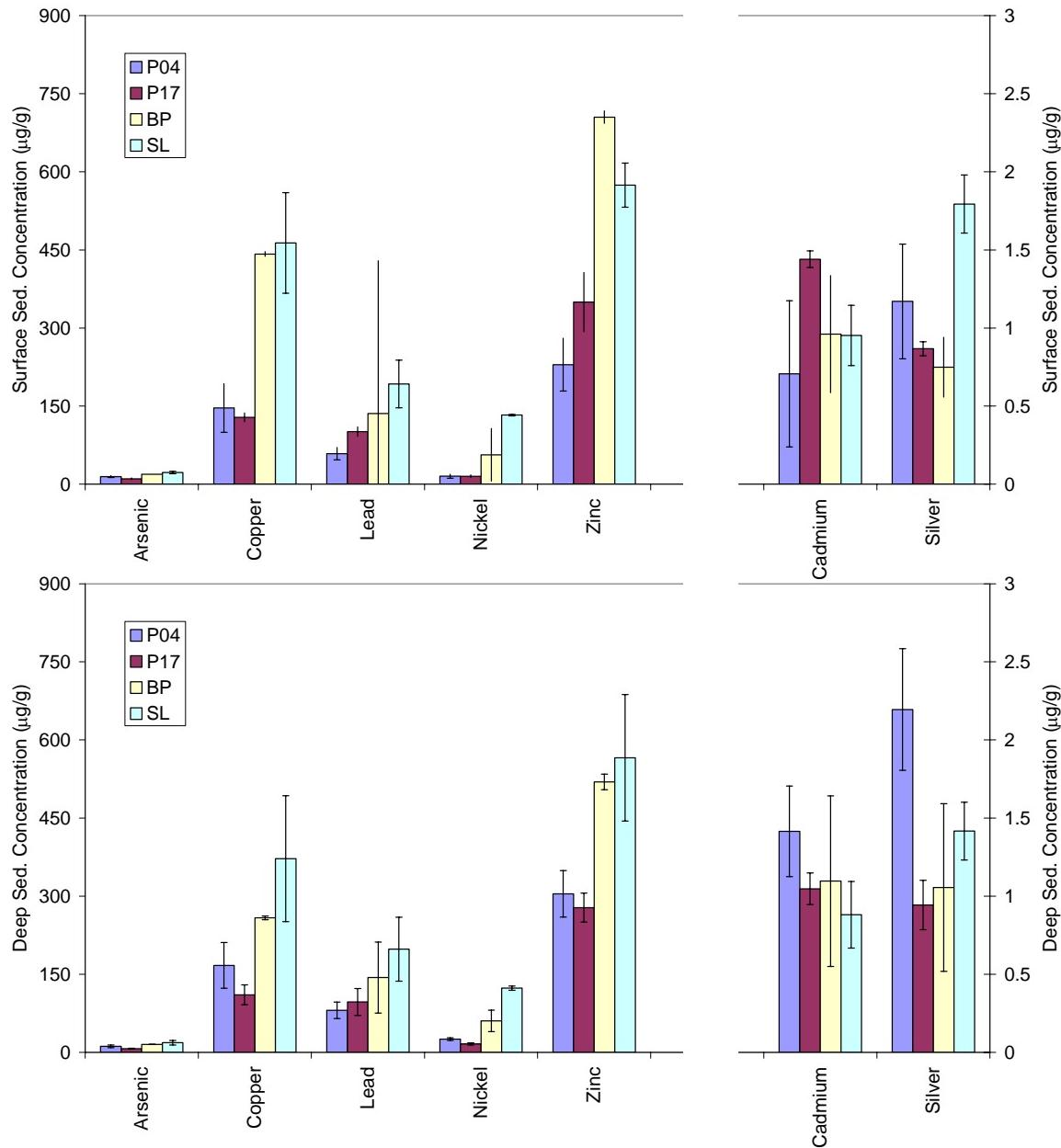


Figure 2-17. Cross-site comparison of surface layer (upper) and deep layer (lower) metal concentrations. Note scale change for different groupings of metals on the left vs. the right.

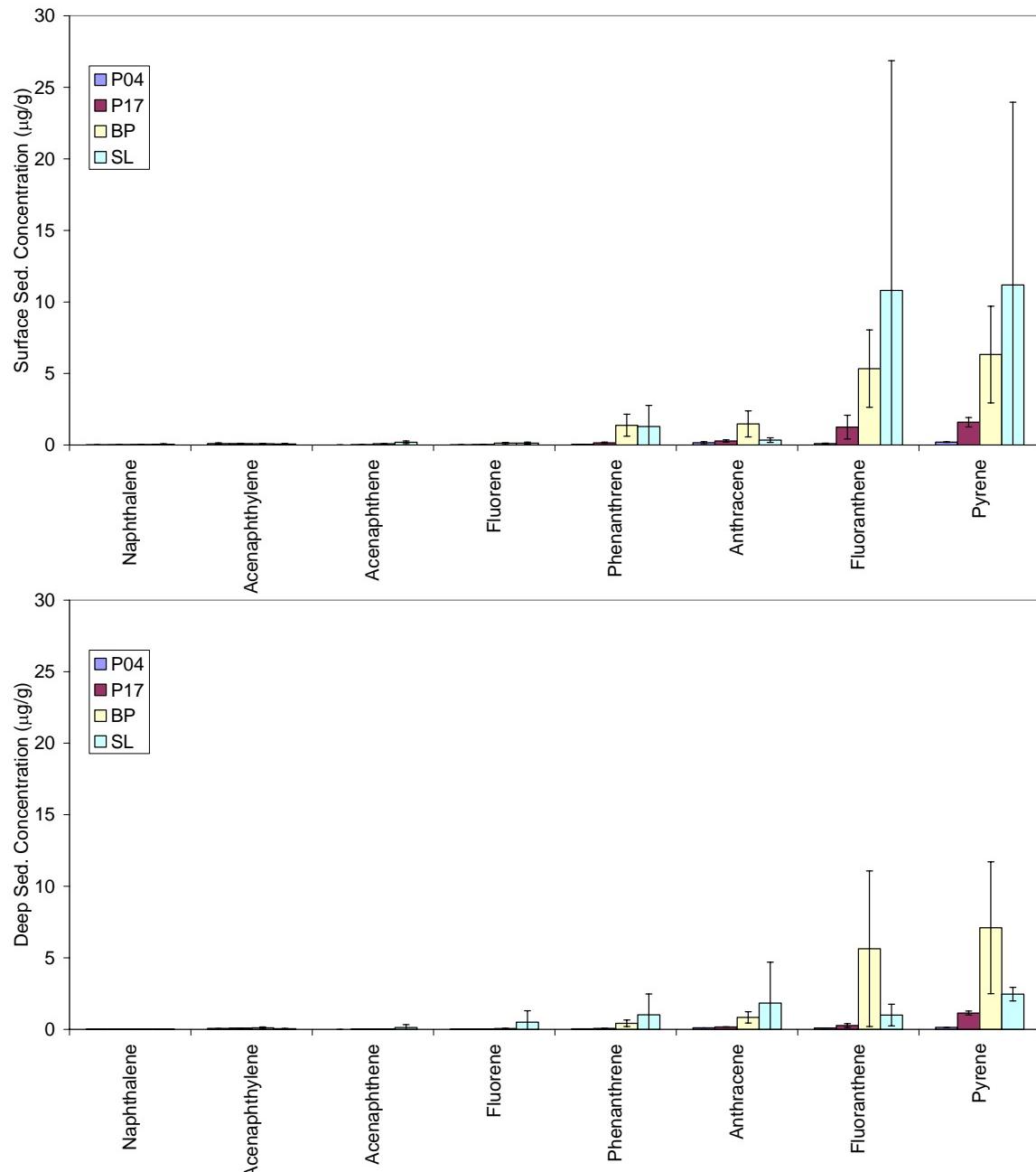


Figure 2-18. Cross-site comparison of surface layer (upper) and deep layer (lower) PAH concentrations.

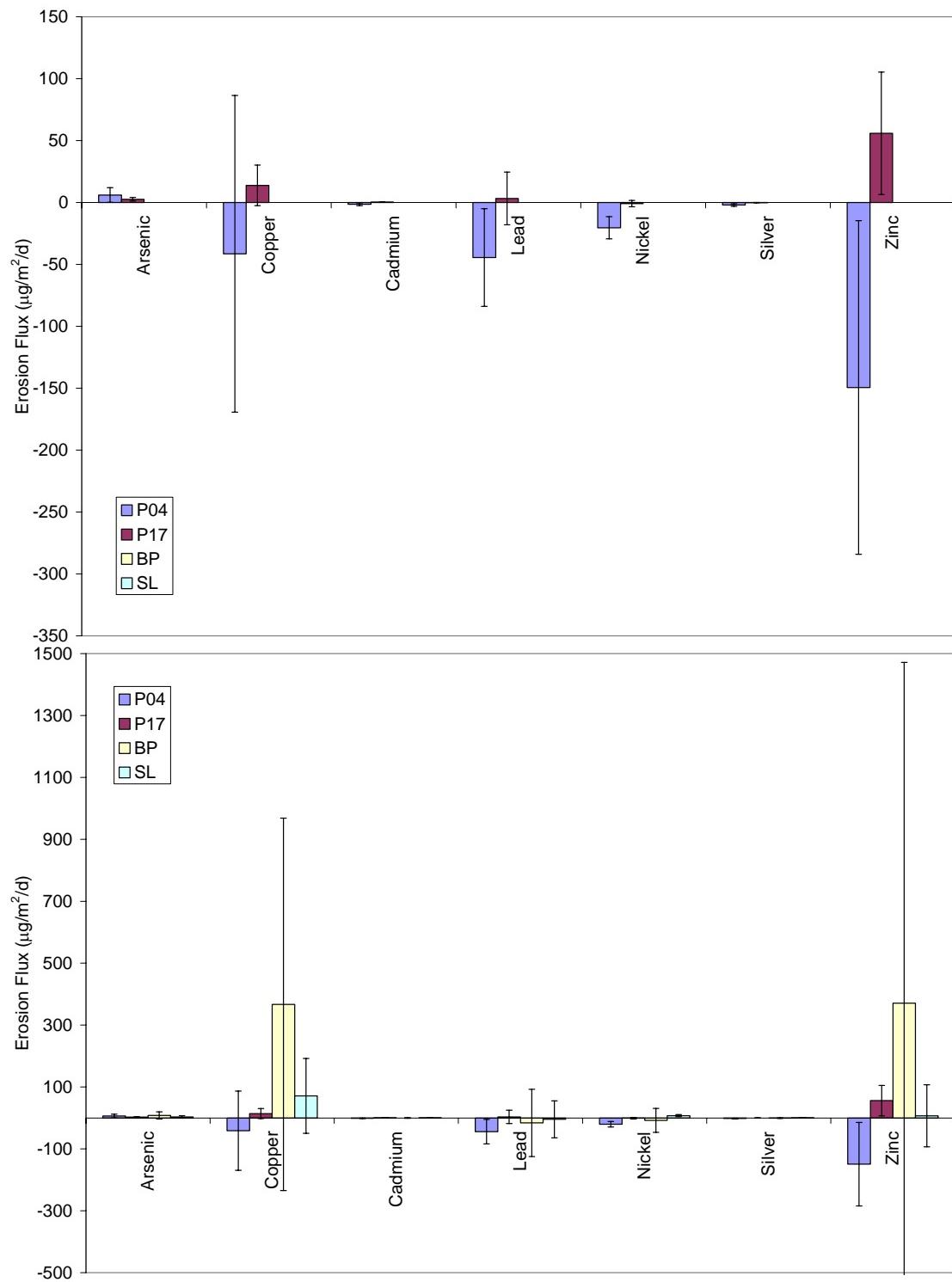


Figure 2-19. Cross-site comparison of erosion fluxes for metals. Upper panel is predicted erosion flux based on measured shear at both sites. Lower panel is potential erosion assuming the same net erosion at Peal stations as measured for Paleta stations. Positive fluxes indicate export from the surface sediment mixed layer.

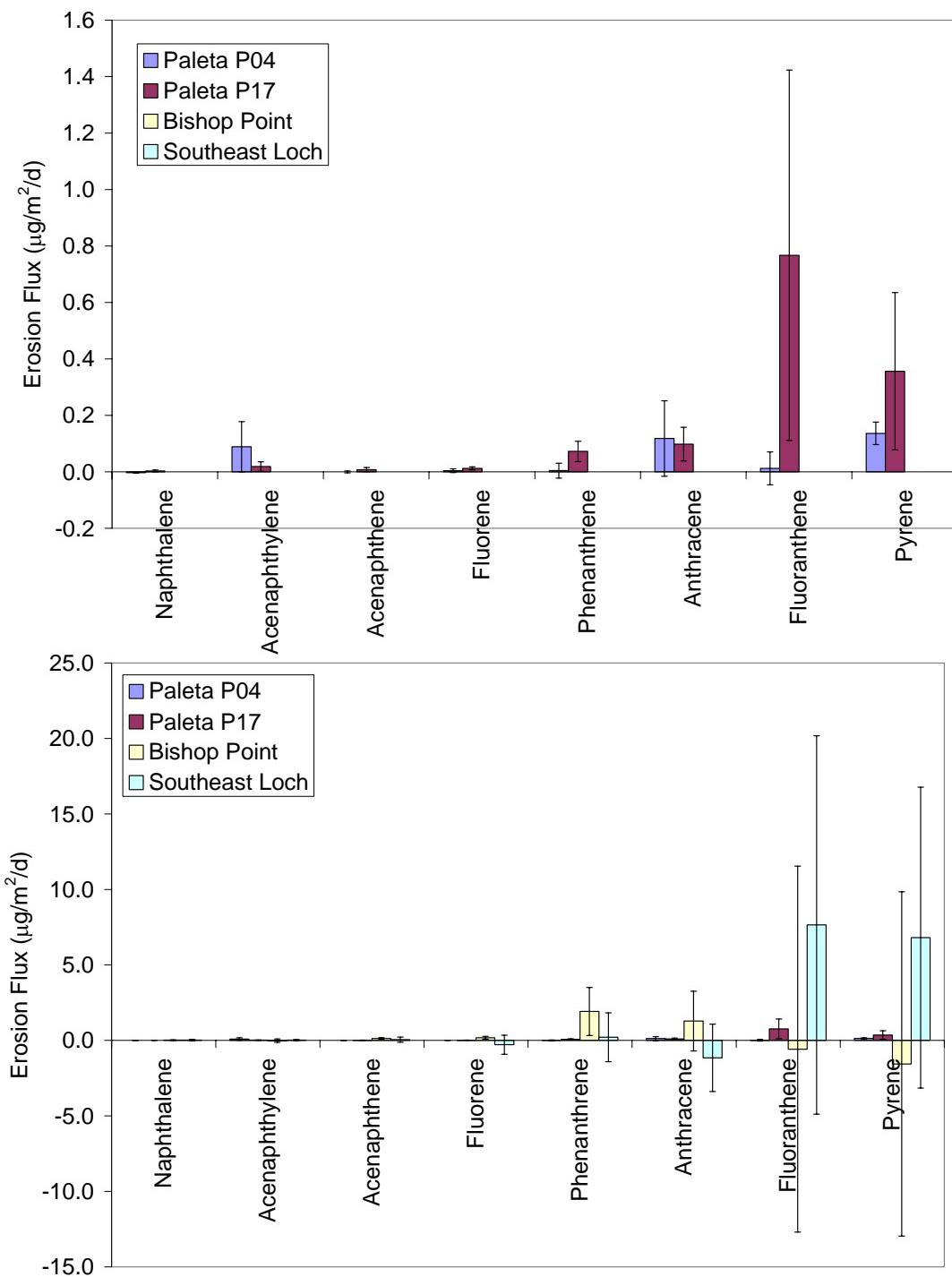


Figure 2-20. Cross-site comparison of erosion fluxes for PAHs. Upper panel is predicted erosion flux based on measured shear at both sites. Lower panel is potential erosion assuming the same net erosion at Peal stations as measured for Paleta stations. Positive fluxes indicate export from the surface sediment mixed layer.

## 2.7 FLUX BY BIODEGRADATION

Fluxes associated with biodegradation were evaluated from core profiles of measured short-term mineralization rates ( $R_D$ ) of radio labeled additions to site sediments. Mineralization rate measurements were limited to three PAHs: naphthalene, phenanthrene and fluoranthene. The biodegradation flux for all PAHs was estimated in two ways. The first estimate was made from the core profiles and mixing depth by calculating the integral-average mineralization rate over the mixed layer depth (H) as

$$F_B = \int_0^H R_D(z) dz \quad (6)$$

This estimate is based on the assumption that aerobic biodegradation of PAHs occurs within the mixed layer at the measured rates as a function of depth. The second estimate was made from only the measured surface mineralization rate ( $R_{DSURF}$ ) and applied to the measured oxygen penetration depth ( $H_{O_2}$ ) as

$$F_B = H_{O_2} R_{DSURF} \quad (7)$$

The second estimate is based on the assumption that aerobic biodegradation at the rates measured will only occur in the presence of oxygen within the sediment column. Alternatively, this estimate could be viewed to be based on the assumption that the time that a mixed layer particle spends in the aerobic zone is proportional to the ratio of the aerobic layer depth to the mixed layer depth. Biodegradation fluxes were calculated for each station at each site based on the equations above. The site-mean flux was then calculated as the average of the station fluxes within the site. Results for the biodegradation fluxes are shown in Figure 2-21.

It was assumed that instantaneous assays reflect *in situ* rates, and that mineralization rates for labeled PAHs reflect rates in sediments. The surface mineralization estimates are probably conservative, as they do not take into account deeper degradation potential observed at sites, particularly as might be stimulated by burrows, but the depth-integrated estimates are most likely over-estimates, as it is unlikely that aerobic degradation is occurring at all times throughout the layer. In addition, essentially one time point was evaluated and is being extrapolated to annual PAH transport and degradation. Extrapolation of these measurements to longer time frames and across larger sediment study sites will likely reduce their relevance to describing *in situ* conditions, but this is a limitation of all necessary field work. Confidence in our understanding of PAH transport and biodegradation in marine sediments grows with iteration of these field measurements seasonally and over different ecosystems.

Cross-site comparison for the two demo sites was evaluated based on comparison of the site-average degradation flux rates for both the depth-integrated assumption and the surface layer assumption. In general, both sites showed a similar pattern in terms of the magnitude of the flux with P>F>N. Depth-integrated mineralization fluxes were generally an order of magnitude higher than near surface fluxes. Fluxes at the Pearl Harbor stations were generally higher than those at Paleta Creek, with the exception of Fluoranthene which was higher at P04. This is

consistent with the generally higher level of PAHs present in Pearl Harbor. When the sites and stations are further compared, elevated measured bacterial mineralization of the PAHs naphthalene, phenanthrene, and fluoranthene were found to associate with areas of the sediment that appear to be more bioturbated based on analyses using the SPI camera and microprofiler data (i.e. P04 and SL).

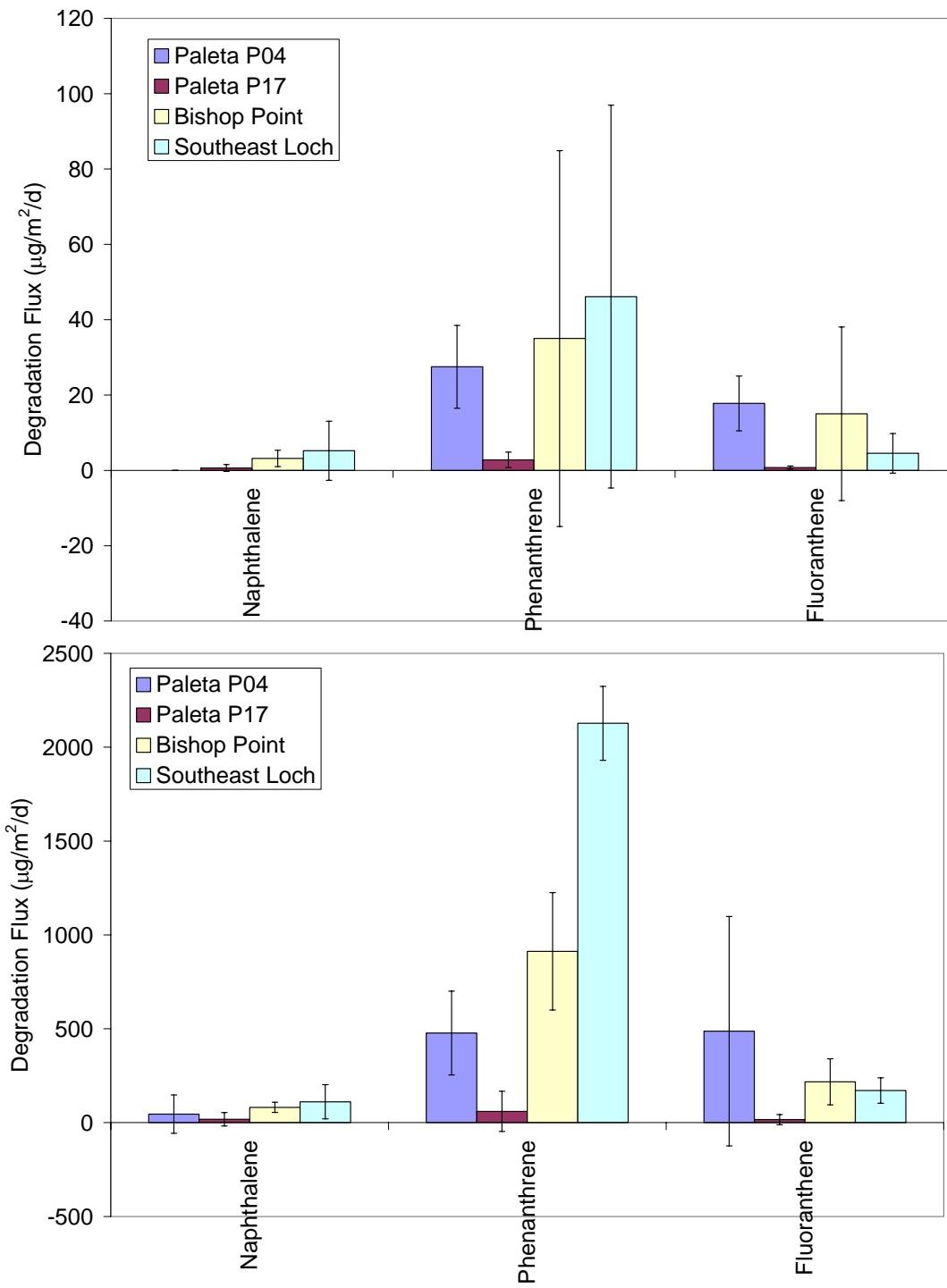


Figure 2-21. Cross-site comparison of degradation fluxes for PAHs. Upper panel is the predicted flux assuming biodegradation only acts in the oxygenated layer. Lower panel is potential flux assuming biodegradation acts throughout the mixed layer. Positive fluxes indicate export from the surface sediment mixed layer.

## 2.8 COMPARATIVE PATHWAY ANALYSIS FOR METALS

Comparative PRISM pathway analysis for metals at Paleta Creek and Pearl Harbor was carried out by comparing the raw flux rates associated with each pathway. The analysis provides a means of evaluating which pathways may be dominant for the given site where the measurements were conducted. The primary pathways that were evaluated for metals at each site included

- Diffusive Flux
- Advective Flux
- Sedimentation Flux
- Erosion Flux

Results are presented below for individual metals that were identified as COPCs at the initiation of the study.

### Arsenic

Overall, the magnitude of pathway fluxes for arsenic followed a pattern of Advection=Settling>Diffusion>Erosion. Pathway analysis for arsenic indicates that dissolved contaminant processes (advection and diffusion) are leading to a loss of arsenic in the surface layer at both sites (Figure 2-22), with the exception of advection at BP. Particle processes (sedimentation and erosion) were generally dominated by sedimentation at both sites. However, the sites show opposing patterns for sedimentation with mass loss at the Pearl Harbor sites, and mass gain to the surface layer for the Paleta Creek sites. Variability as quantified by within station (Paleta) or within strata (Pearl) replication was of similar magnitude for Arsenic fluxes at the two sites. An examination of all fluxes suggests that the surface mixed layer may be experiencing a net loss of Arsenic as the sum of all processes, with this flux dominated by advection at the Paleta stations, and by settling at the Pearl stations.

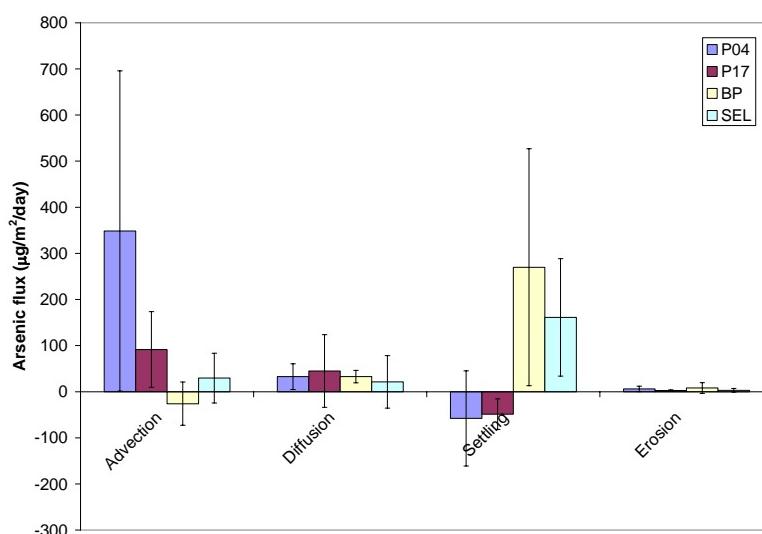


Figure 2-22. PRISM pathway fluxes for arsenic.

## Copper

Overall, the magnitude of pathway fluxes for copper indicated a pattern dominated by settling fluxes (Figure 2-23). Fluxes associated with advection, diffusion and erosion were all negligible relative to settling. At Paleta Creek, settling fluxes at both stations suggest mass gain of Copper in the surface mixed layer, while for Pearl, SL showed a mass gain and BP showed a mass loss due to settling. Variability as quantified by within station (Paleta) or within strata (Pearl) replication was significantly higher for the larger spatial separations associated with the strata design at Pearl Harbor. The high variability in the Peal Harbor strata suggests that, over these spatial scales, processes and associated fluxes may vary to the extent that different pathway rankings could emerge depending on what area of the strata was examined. An examination of all fluxes suggests that the surface mixed layer may be experiencing a net gain of Copper as the sum of all processes at all areas except Bishop Point, with the flux dominated by settling. This pattern is consistent with ongoing activities in the Paleta Creek and Southeast Loch areas including use of antifouling coatings, shipyard operations, and stormwater discharges. These sources are not present to the same degree at Bishop Point.

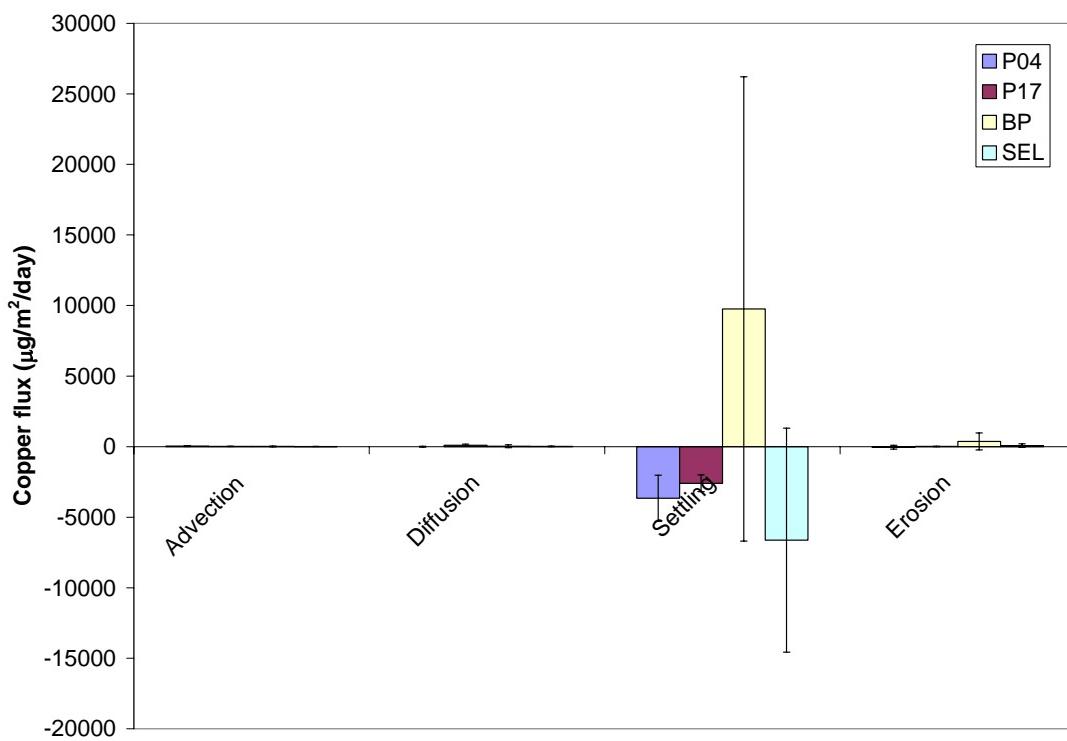


Figure 2-23. PRISM pathway fluxes for copper.

## Cadmium

Overall, the magnitude of pathway fluxes for cadmium followed a pattern of Settling>Advection=Diffusion>Erosion (Figure 2-24). Pathway analysis for cadmium indicates that dissolved contaminant processes (advection and diffusion) are generally leading to a loss of Cd in the surface layer at both sites, although the variability is very high, especially for diffusion. The advection pathway at Pearl Harbor was negligible relative to Paleta. At Pearl Harbor, settling fluxes at both stations suggest mass loss of cadmium in the surface mixed layer, while for Paleta, P04 showed a mass loss and P17 showed a mass gain due to settling. Variability as quantified by within station (Paleta) or within strata (Pearl) replication was of similar magnitude for cadmium fluxes at the two sites. An examination of all fluxes suggests that the surface mixed layer at both sites may be experiencing a net loss of cadmium as the sum of all processes, dominated by settling, with the exception of Paleta station P17 where results suggest a net gain dominated by settling. This difference at P17 is related to the station proximity to the mouth of Paleta Creek and associated release from storm events.

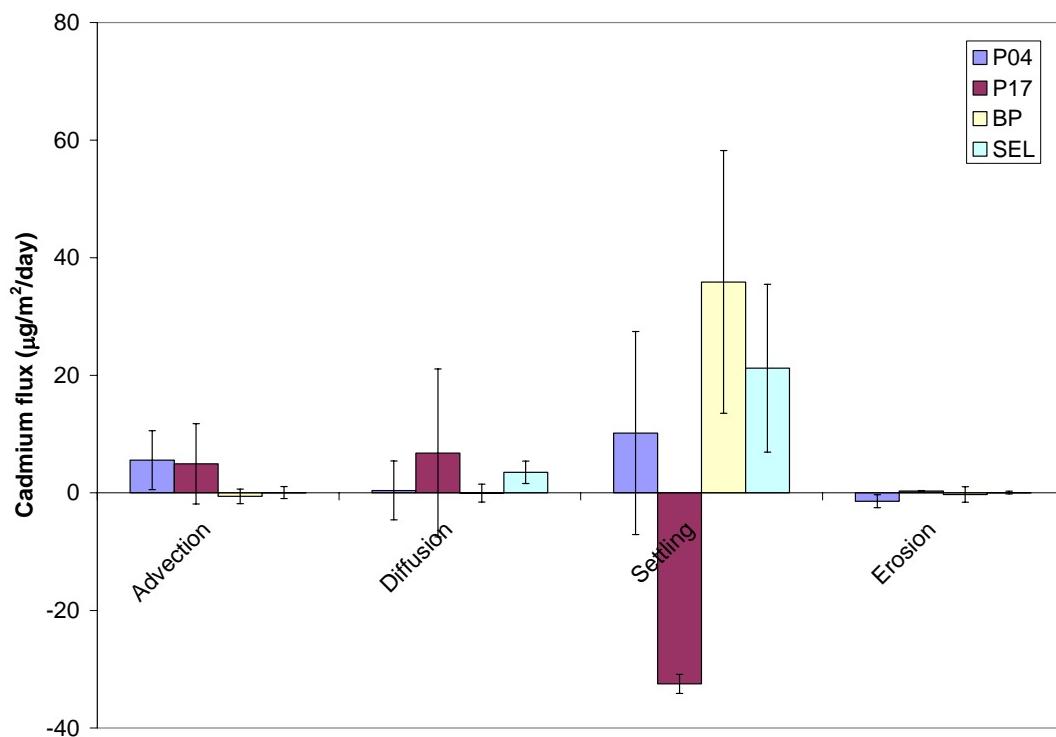


Figure 2-24. PRISM pathway fluxes for cadmium.

## Lead

Pathway analysis for lead indicates that variations in surface layer concentrations at both sites are strongly dominated by settling fluxes (Figure 2-25). Fluxes associated with advection, diffusion and erosion were all negligible relative to settling. Settling fluxes for lead at Paleta Creek are acting as a continuing source to the surface layer, while at Pearl Harbor they are driving a mass loss from the surface layer. Variability as quantified by within station (Paleta) or within strata (Pearl) replication was significantly higher for the larger spatial separations associated with the strata design at Pearl Harbor. The high variability in the Peal Harbor strata suggests that, over these spatial scales, processes and associated fluxes may vary to the extent that different pathway rankings could emerge depending on what area of the strata was examined. An examination of all fluxes suggests that the surface mixed layer may be experiencing a net gain of lead as the sum of all processes at Paleta Creek areas, and a net loss of lead at Pearl harbor areas, with the fluxes at both sties dominated by settling. This pattern is consistent with ongoing stormwater sources in the Paleta Creek area. It appears these sources are not as prevalent at the Pearl Harbor sites.

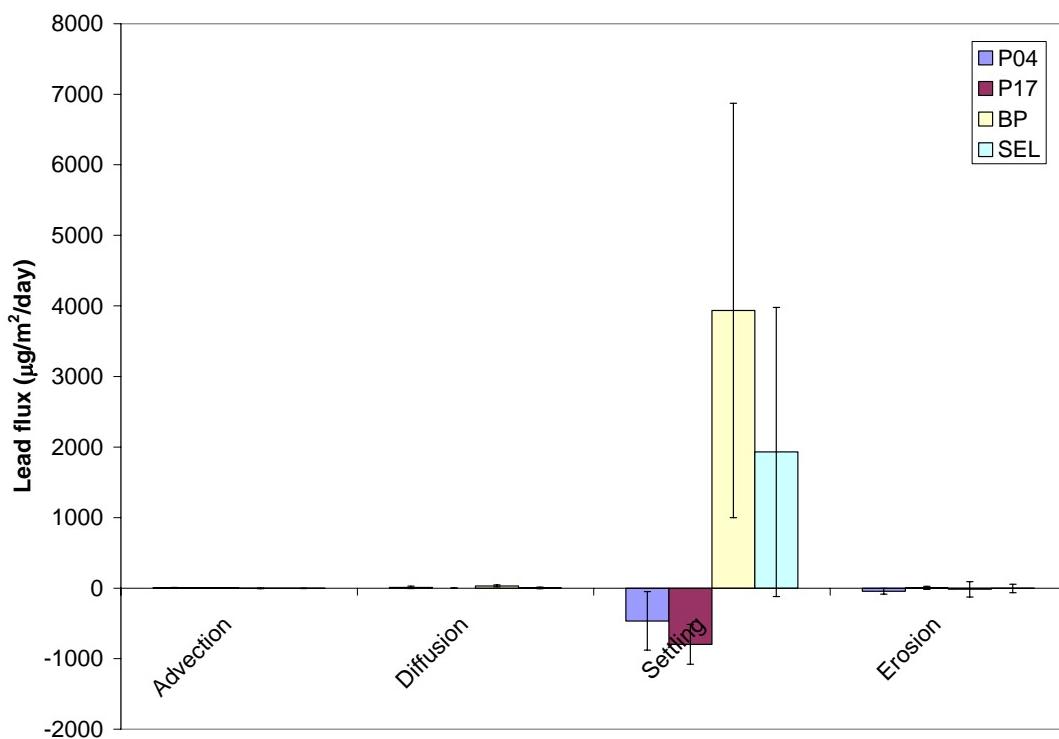


Figure 2-25. PRISM pathway fluxes for lead.

## Nickel

Overall, the magnitude of pathway fluxes for nickel followed a pattern of Settling=Advection>Diffusion>Erosion (Figure 2-26). Diffusive fluxes at the two sites were of comparable magnitude and generally indicate mass loss of nickel from the surface layer. Advective fluxes at Pearl Harbor were significantly higher in magnitude and appear to act as a source to the surface layer, in contrast to Paleta Creek where these fluxes generally indicate a mass loss from the surface sediments. Differences in advective fluxes at the two sites could be linked to different approaches for determining the deep layer porewater concentration that were used. Settling fluxes showed the opposite pattern as advective fluxes, with settling leading to mass loss in the surface sediments at Paleta Creek and mass gain in the surface sediments at Pearl Harbor. Variability as quantified by within station (Paleta) or within strata (Pearl) replication was significantly higher for the larger spatial separations associated with the strata design at Pearl Harbor. The high variability in the Peal Harbor strata suggests that, over these spatial scales, processes and associated fluxes may vary to the extent that different pathway rankings could emerge depending on what area of the strata was examined. An examination of all fluxes suggests that Ni concentrations in the surface layer may be near steady state, with Paleta Creek sediments balanced by losses from advection and diffusion and gain from settling, and Pearl harbor sediments balanced by gain from advection and loss from diffusion and settling.

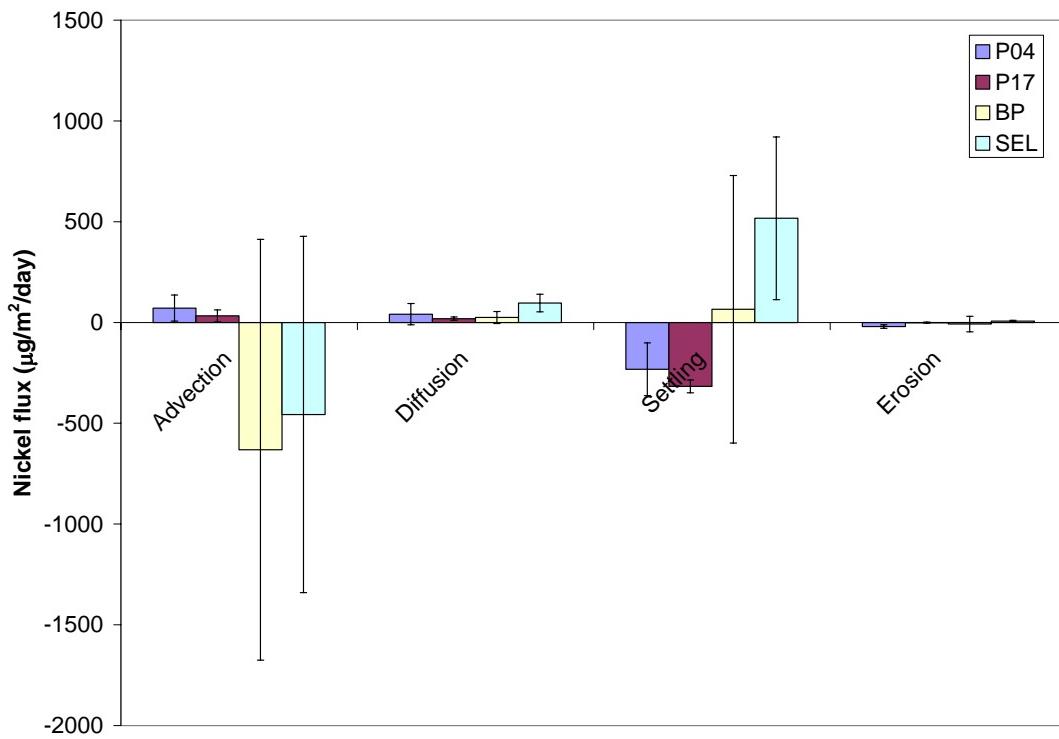


Figure 2-26. PRISM pathway fluxes for nickel.

## Silver

Pathway analysis for silver indicates that variations in surface layer concentrations at both sites are strongly dominated by settling fluxes (Figure 2-27). Fluxes associated with advection, diffusion and erosion were generally negligible relative to settling, except at P17. Settling fluxes showed no clear pattern between the two sites, with both positive and negative mean fluxes at both harbors. Results suggest settling is an ongoing source of silver to the surface sediments at P04 and Bishop Point, as opposed to Southeast Loch where the settling acts to reduce silver in the surface layer, and P17 where the settling flux is relatively small. Variability as quantified by within station (Paleta) or within strata (Pearl) replication was of similar magnitude for silver fluxes at the two sites, except for settling at BP where the replicate variability exceeded other areas by about an order of magnitude. An examination of all fluxes suggests that the surface mixed layer response for silver showed no clear pattern across sites, with net gain, net loss, or near steady state conditions occurring at various stations. The net loss or near steady state conditions observed at P17 and Southeast Loch are interesting from the standpoint that these areas are generally closer to industrial and non-point sources than the other two sites. This difference may indicate that the net gain of silver at P04 and Bishop Point results from transport from other areas as opposed to local sources.

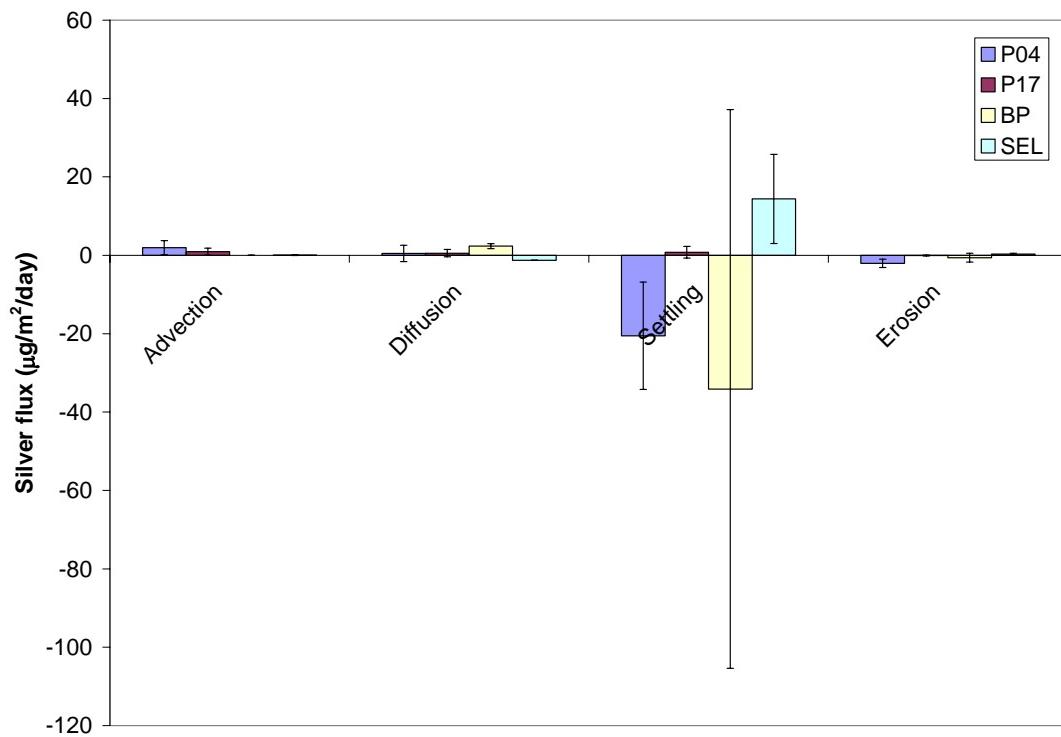


Figure 2-27. PRISM pathway fluxes for silver.

## Zinc

Overall, the magnitude of pathway fluxes for zinc followed a pattern of Settling>Advection=Diffusion>Erosion (Figure 2-28). Pathway analysis for zinc indicates that dissolved contaminant processes (advection and diffusion) are generally leading to a loss of zinc in the surface layer at both sites. The advection and diffusion pathways were generally stronger at Pearl Harbor relative to Paleta. At Paleta Creek, settling fluxes at both stations suggest mass gain of zinc in the surface mixed layer, while for Pearl Harbor, Bishop Point showed a mass loss and Southeast Loch showed a mass gain due to settling. This pattern is similar to the pattern observed to copper, and these are metals that commonly co-occur in both industrial sources and non-point source. Variability as quantified by within station (Paleta) or within strata (Pearl) replication was significantly higher for the larger spatial separations associated with the strata design at Pearl Harbor. The high variability in the Peal Harbor strata suggests that, over these spatial scales, processes and associated fluxes may vary to the extent that different pathway rankings could emerge depending on what area of the strata was examined. An examination of all fluxes suggests that the surface mixed layer may be experiencing a net gain of zinc as the sum of all processes at all areas except Bishop Point, with the flux dominated by settling. This pattern is consistent with ongoing activities in the Paleta Creek and Southeast Loch areas including use of antifouling coatings, shipyard operations, and stormwater discharges. These sources are not present to the same degree at Bishop Point.

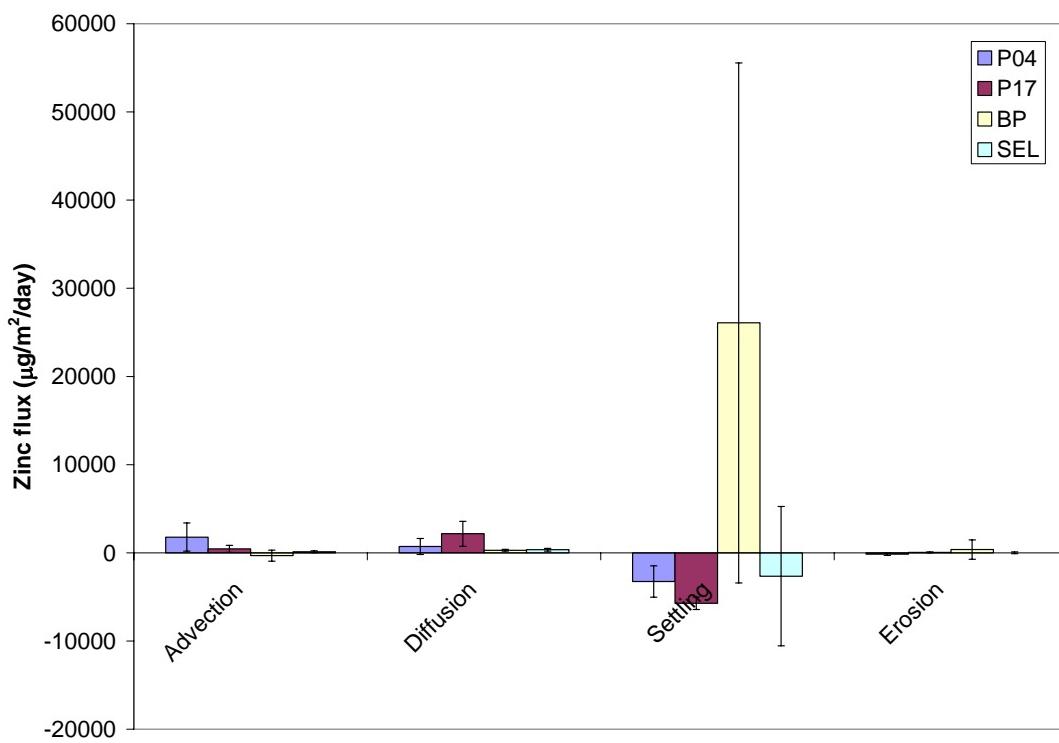


Figure 2-28. PRISM pathway fluxes for zinc.

## **2.9 COMPARATIVE PATHWAY ANALYSIS FOR PAHS**

The PRISM pathway analysis for PAHs at Paleta Creek and Pearl Harbor was carried out by comparing the raw flux rates associated with each pathway. The analysis provides a means of evaluating which pathways may be dominant for the given site where the measurements were conducted. The primary pathways that were evaluated for metals at each site included

- Diffusive Flux
- Advective Flux
- Sedimentation Flux
- Erosion Flux
- Biodegradation Flux (surface and depth-integrated)

Results are presented below for the individual PAHs naphthalene, phenanthrene and fluoranthene, for which all processes were measured.

### **Naphthalene**

Pathway analysis for naphthalene was examined comparing the two biodegradation assumptions (depth-integrated and surface layer; Figure 2-29). Applying the depth-integrated degradation flux, the pathway analysis indicates that variations in surface layer concentrations at both sites were dominated by biodegradation fluxes. Relative to the depth-integrated biodegradation, surface mineralization, settling, advection, diffusion and erosion were all negligible at both sites. Biodegradation fluxes were generally stronger at the Pearl Harbor stations than at Paleta Creek.

If only surface mineralization is considered, then other processes become important as well. Comparative differences across sites are dominated by the large advective flux from the surface layer at Southeast Loch in Pearl Harbor. Southeast Loch also had the strongest mean degradation rate. The strong mass flux of naphthalene from the surface sediment layer due to advection at this station is somewhat anomalous because all other PAHs showed an increasing concentration profile with depth, leading to mass gain in the surface layer as a result of positive mean advection. With the exception of advection at Southeast Loch, degradation and settling were the dominant pathways for naphthalene, followed by diffusion. Variability as quantified by within station (Paleta) or within strata (Pearl) replication was significantly higher for the larger spatial separations associated with the strata design at Pearl Harbor. The high variability in the Pearl Harbor strata suggests that, over these spatial scales, processes and associated fluxes may vary to the extent that different pathway rankings could emerge depending on what area of the strata was examined.

Whether surface mineralization or depth-integrated mineralization is the more relevant process to apply to the sediments to determine mineralization flux is not clear. Most researchers have only found aerobic mineralization in the shallow surface layer in which oxygen penetrates. However, this study found evidence of instantaneous aerobic mineralization rates in some samples to a depth of several cm, especially in the more bioturbated cores at P04 and SL. Oxygen microprofiles also showed some cases of deeper oxygen penetration, especially around burrows. Most likely, degradation fluxes lie somewhere between these two estimates. An examination of all fluxes suggests that, if biodegradation of naphthalene is active throughout the surface mixed layer (depth H), then rapid mass loss could be expected, whereas if only the shallow aerobic

layer is active, then losses due to biodegradation may be balanced to some extent by gains from settling and diffusion.

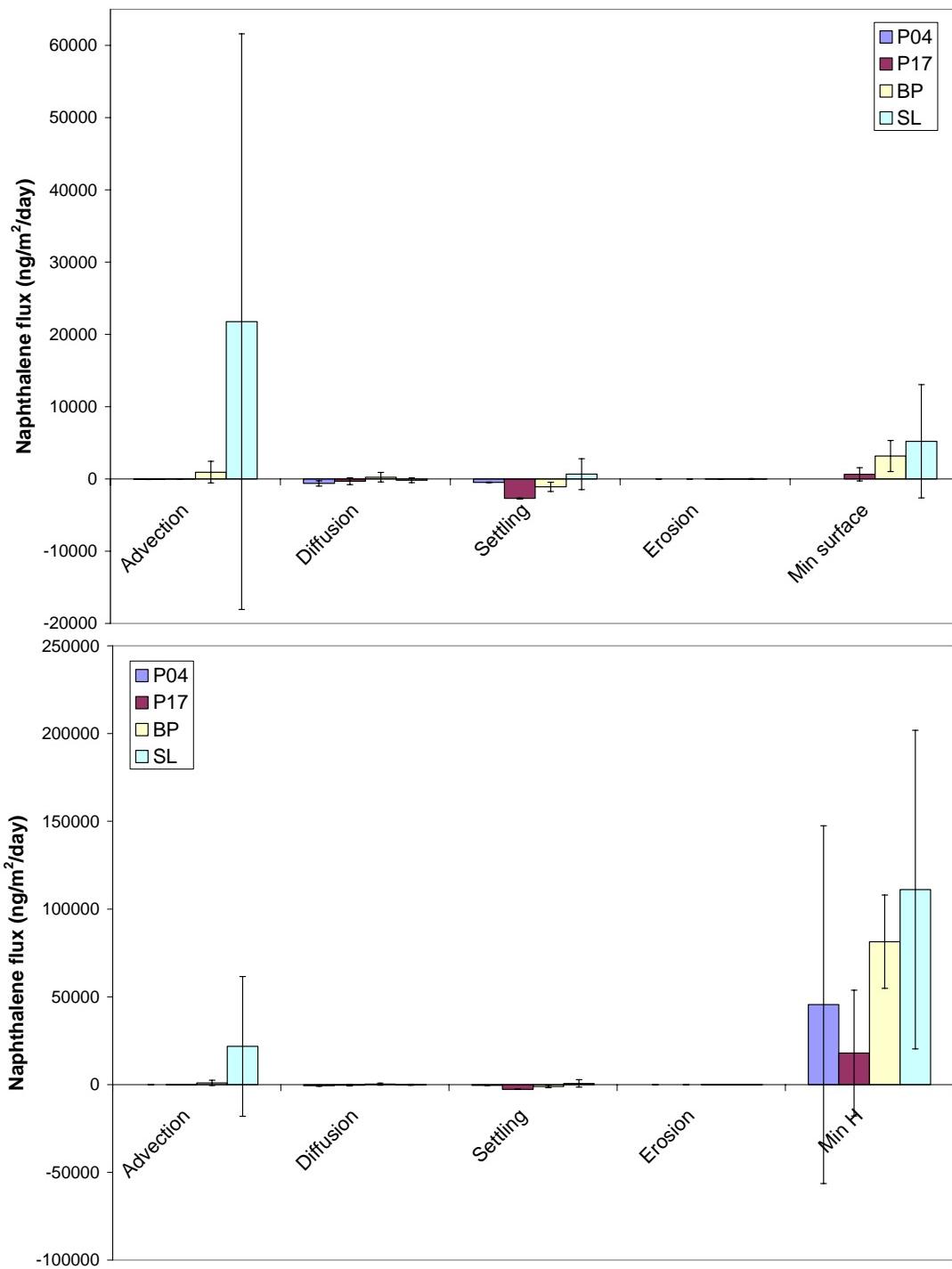


Figure 2-29. PRISM pathway fluxes for naphthalene including comparison for depth-integrated biodegradation (top) and without it (bottom).

## **Phenanthrene**

Pathway analysis for phenanthrene was examined comparing the two biodegradation assumptions (depth-integrated and surface layer; Figure 2-30). Applying the depth-integrated degradation flux, the pathway analysis indicates that variations in surface layer concentrations at both sites were dominated by biodegradation fluxes, although to a lesser extent at P17. Relative to the depth-integrated biodegradation, surface mineralization, settling, advection, diffusion and erosion were all negligible at both sites, with the exception of settling at Bishop Point. Biodegradation fluxes for phenanthrene were generally stronger at the Pearl Harbor stations than at Paleta Creek.

If only surface mineralization is considered, then other processes become important as well. Comparative differences across sites are dominated by the large settling flux to the surface layer at Bishop Point in Pearl Harbor. At other sites (i.e. P04 and SL), results indicate a rough balance between settling as a source, and degradation as a loss from the surface layer. Advection and diffusion fluxes were generally low and variable across the two sites. Variability as quantified by within station (Paleta) or within strata (Pearl) replication was generally higher for the larger spatial separations associated with the strata design at Pearl Harbor. The high variability in the Pearl Harbor strata suggests that, over these spatial scales, processes and associated fluxes may vary to the extent that different pathway rankings could emerge depending on what area of the strata was examined.

Whether surface mineralization or depth-integrated mineralization is the more relevant process to apply to the sediments to determine mineralization flux is not clear. Most researchers have only found aerobic mineralization in the shallow surface layer in which oxygen penetrates. However, this study found evidence of instantaneous aerobic mineralization rates in some samples to a depth of several cm, especially in the more bioturbated cores at P04 and SL. Oxygen microprofiles also showed some cases of deeper oxygen penetration, especially around burrows. Most likely, degradation fluxes lie somewhere between these two estimates. An examination of all fluxes suggests that, if biodegradation of phenanthrene is active throughout the surface mixed layer (depth H), then rapid mass loss could be expected, whereas if only the shallow aerobic layer is active, then losses due to biodegradation may be balanced to some extent by gains from settling, except at Bishop Point where the balance would be dominated by settling as a source to the surface layer.

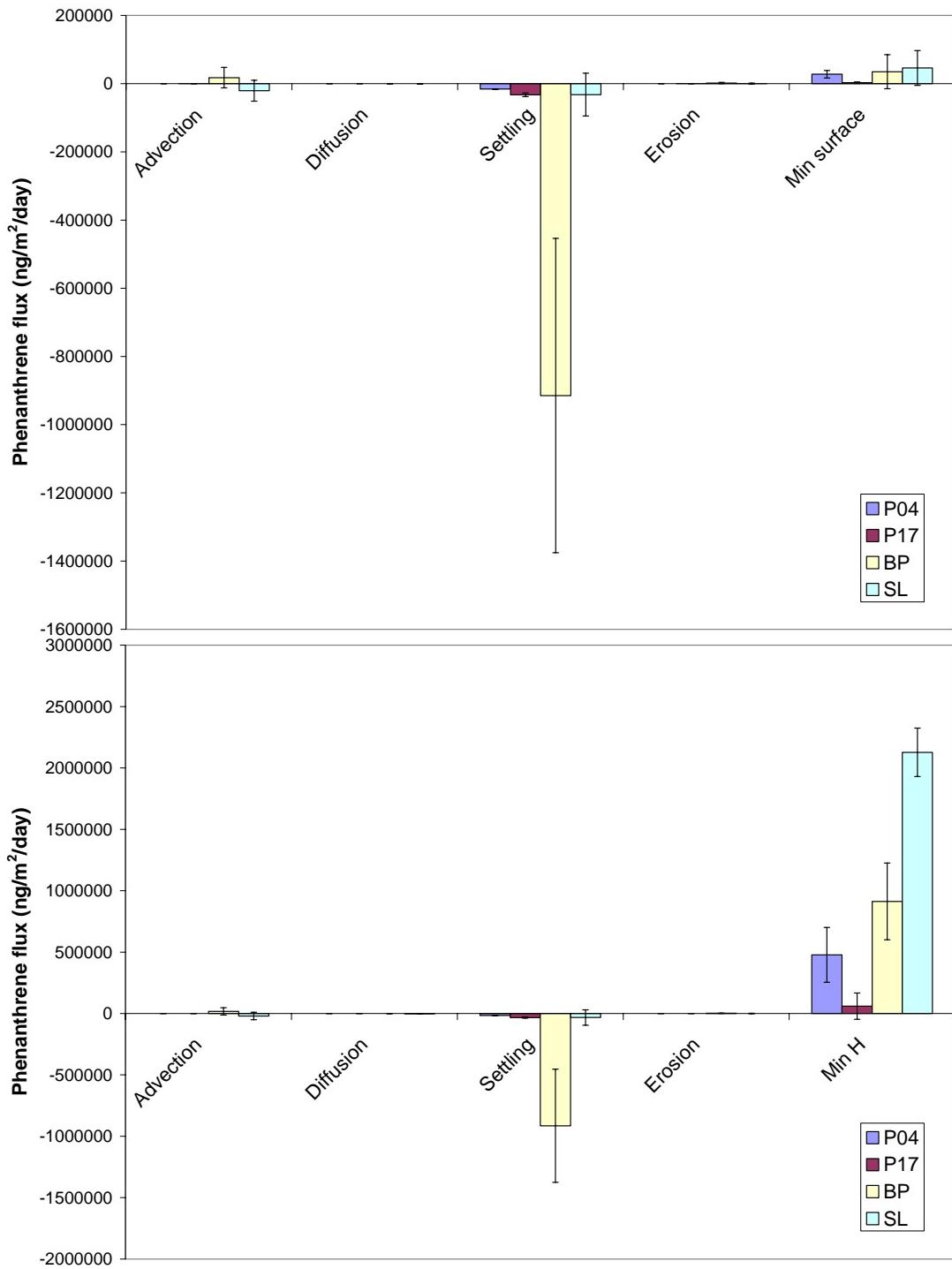


Figure 2-30. PRISM pathway fluxes for phenanthrene including comparison for depth-integrated biodegradation (top) and without it (bottom).

## **Fluoranthene**

Pathway analysis for fluoranthene was examined comparing the two biodegradation assumptions (depth-integrated and surface layer; Figure 2-31). Applying the depth-integrated degradation flux, the magnitude of pathway fluxes for fluoranthene followed a pattern of Settling=Biodegradation>Advection>Diffusion=Erosion. Biodegradation fluxes at the Pearl harbor stations were comparable to each other and fell between the range of the higher flux observed at P04, and the lower flux at P17. In contrast, settling fluxes at Paleta Creek stations were comparable to each other and indicated a low-level source to the surface layer, while settling fluxes at the two Pearl stations varied widely from strong source loading at Bishop Point, to mass loss at Southeast Loch. Relative to the depth-integrated biodegradation and settling, advection, diffusion and erosion were generally low at both sites, with the exception of a significant advective source at Southeast Loch. Biodegradation fluxes for fluoranthene were generally stronger at the Pearl Harbor stations than at Paleta Creek.

If only surface mineralization is considered, then biodegradation fluxes are on the same order as advection, diffusion and erosion, and the overall flux is dominated by settling at Pearl Harbor, and is a balance of settling and biodegradation in Paleta Creek. Variability as quantified by within station (Paleta) or within strata (Pearl) replication was generally higher for the larger spatial separations associated with the strata design at Pearl Harbor. The high variability in the Pearl Harbor strata suggests that, over these spatial scales, processes and associated fluxes may vary to the extent that different pathway rankings could emerge depending on what area of the strata was examined.

Whether surface mineralization or depth-integrated mineralization is the more relevant process to apply to the sediments to determine mineralization flux is not clear. Most researchers have only found aerobic mineralization in the shallow surface layer in which oxygen penetrates. However, this study found evidence of instantaneous aerobic mineralization rates in some samples to a depth of several cm, especially in the more bioturbated cores at P04 and SL. Oxygen microprofiles also showed some cases of deeper oxygen penetration, especially around burrows. Most likely, degradation fluxes lie somewhere between these two estimates. An examination of all fluxes suggests that, if biodegradation of fluoranthene is active throughout the surface mixed layer (depth H), then rapid mass loss could be expected at Southeast Loch as a result of dominant biodegradation and settling fluxes. In contrast, at Bishop Point, even assuming mixed layer biodegradation, the ongoing settling source still dominates the pathway balance. If only the shallow aerobic layer is active, then the overall flux at the Pearl Harbor stations would be dominated by loss or gain related to settling, while at Paleta Creek losses due to biodegradation would be balanced to some extent by gains from settling. In general, it appears that pathway rankings for PAHs tend to shift from degradation dominated for the lower molecular weight PAHs (e.g. naphthalene) toward settling dominated for the mid-higher molecular weight PAHs such as fluoranthene.

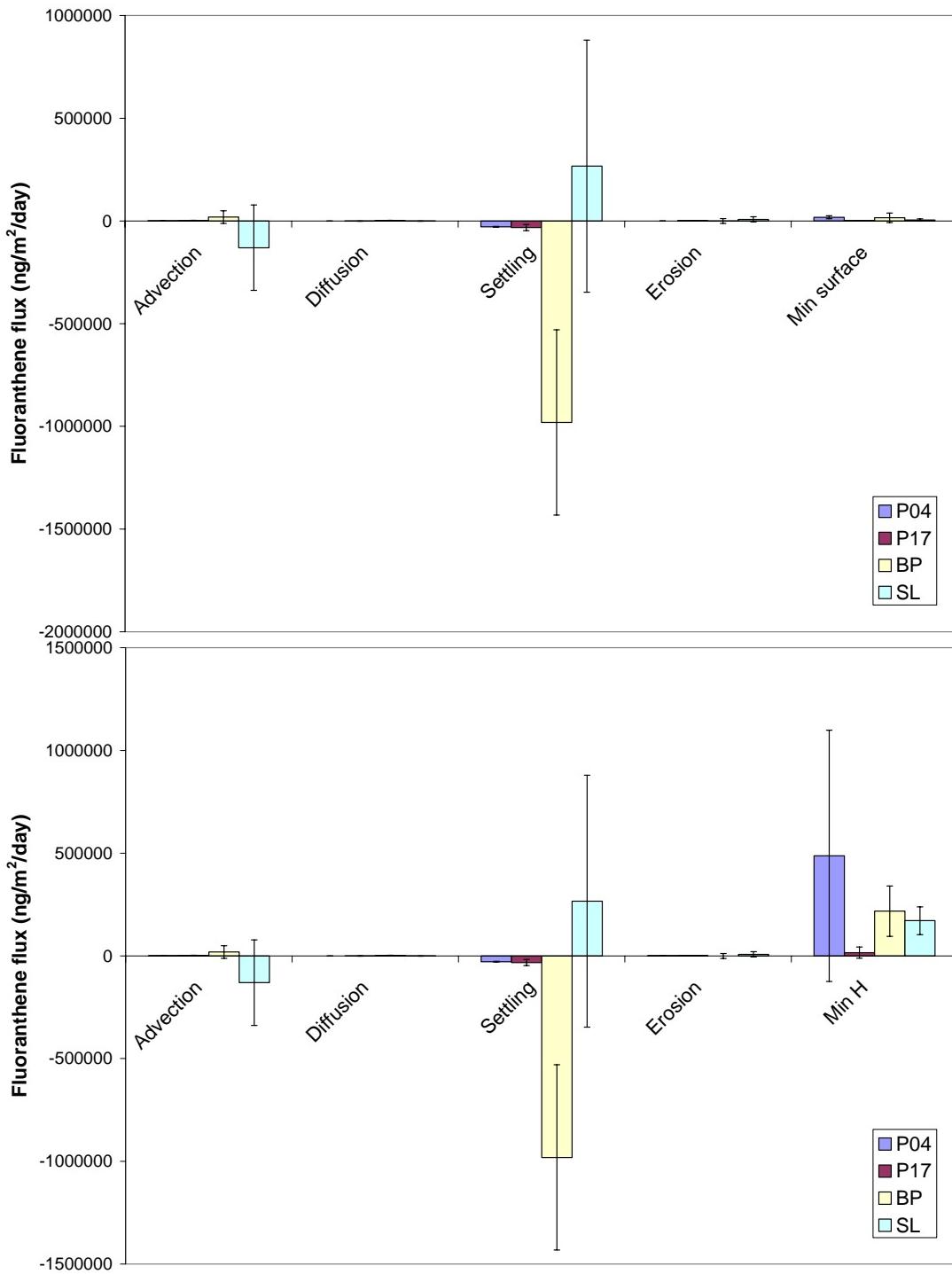


Figure 2-31. PRISM pathway fluxes for fluoranthene including comparison for depth-integrated biodegradation (top) and without it (bottom).

### **3 Summary**

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The objective of this program was to provide an understanding of the relative importance of critical pathways contaminant transport across the sediment/seawater interface in the risk, fate and management of near-shore, in-place contaminated sediments via: 1) An integrated suite of measurement techniques to characterize and quantify important transport pathways for in-place sediments, 2) A corresponding set of indices that quantify the transport phenomenon on a common dimensional scale and 3) Field scale evaluation of the effectiveness of the measurement tools and the importance of quantified transport pathways.

The program was successful at two Navy harbors in fielding the measurement suite, and quantifying a range of process-based transport pathways including:

- Diffusive Fluxes
- Advective Fluxes
- Sedimentation Fluxes
- Erosion Fluxes
- Biodegradation Fluxes

The PRISM pathway analysis provided a means of evaluating general differences between the two areas in San Diego Bay and Pearl Harbor. On a contaminant-specific level, these patterns provided insight into management approaches, and also into those parameters that might warrant further investigation. These pathway flux estimates can provide insight into important management approaches (e.g., source control, capping, recovery). Results can help focus further site studies to most important or uncertain parameters. Flux rates can be utilized in models for predicting exposure risks or recovery rates. General findings from the cross-comparison of the sites are summarized below.

Cross-site comparisons revealed a number of differences and similarities between the study areas in Pearl Harbor and Paleta Creek. Both the mean biological mixing depth and the mean RPD were deeper at the Pearl Harbor sites compared to the San Diego sites. In particular, the time-lapse profile at Southeast Loch showed quite dramatic changes in subsurface feeding void/burrow structure over time that explained the low shear strength and high water content observed in this area, along with the bioirrigation variability detected in the groundwater flux data.

Tidally-averaged specific discharge rates across the two sites were comparable, and the variation among replicates was also comparable, even though the spatial separation at the Pearl Harbor stations was significantly greater than for Paleta Creek. Porewater and surface water metal concentrations for the two sites were of similar magnitude, but showed differing trends for different metals. General agreement between the advective metal fluxes at the two sites was observed for the approximate magnitude and direction of fluxes for As, Cu and Zn. Clear differences were observed for Ni and Pb. These differences appear to hinge on the assumption of low metal concentrations in the deep sediment layer at the Paleta Creek stations. In contrast to metals, porewater and surface water PAH concentrations were significantly different across the two sites, with much higher concentrations at the Pearl Harbor stations relative to the Paleta Creek stations. In general, mixed layer and deep layer porewater concentrations exceeded surface water concentrations at both sites. However, the gradients were significantly higher at the Pearl

Harbor stations, and thus strikingly higher advective fluxes were estimated from the data at Pearl Harbor relative to Paleta Creek.

Cross-site comparison of diffusive metal fluxes for the two sites indicates highest Ni and Pb fluxes at Pearl Harbor stations, highest Cu and Zn fluxes at Paleta Creek, and fairly comparable fluxes of other metals. Mean flux rates for most metals at both sites were positive, indicating a general trend of release of metal from the sediment to the water column by this pathway. Cross-site comparison for the two sites indicates generally similar patterns of diffusive PAH fluxes, with some differences in magnitude, and particularly highest Fluoranthene and Pyrene fluxes at Pearl Harbor.

Sedimentation rates were generally similar across sites, in the range of 1-2 cm/d. These rates are typical of coastal harbors and embayments. Trap sediment metals followed similar general patterns of concentration for the two sites with some notable exceptions such as Cu and Zn at Southeast Loch, and Cu, Zn and Cd at P17. For the surface sediments, metals were generally higher at the Pearl Harbor stations compared to Paleta Creek, particularly Cu and Zn. Cross-site comparison indicates that settling fluxes at Paleta Creek were consistently negative (source to the surface layer) and of lower magnitude when compared to Pearl Harbor stations. For Southeast Loch, Cu and Zn settling added to the surface sediment mass, while in contrast, Bishop Point results indicated strong positive fluxes for most metals indicating a general reduction in surface sediment loading as a result of settling. Trap and surface sediment PAHs followed similar general trends of concentration for the two demo sites with higher concentrations for higher molecular weight PAHs (e.g. Fluoranthene and Pyrene). PAHs were significantly higher in the Bishop Point traps, while trap concentrations at P17 and Southeast Loch were moderate and comparable, and P04 concentrations were consistently the lowest. For the surface sediments, PAHs were consistently higher at the Pearl Harbor stations compared to Paleta Creek. For PAHs, settling fluxes at both sites for most PAHs indicated settling as a source to the surface layer, with the exception of the heavier molecular weight PAHs at Southeast Loch. Settling fluxes (whether positive or negative) were generally of higher magnitude at Pearl Harbor, consistent with the stronger contaminant gradients observed in the traps and sediments.

Critical shear stress was found to be the same value in both replicates at both Paleta Creek sites, while critical shear stress at the Pearl Harbor stations was generally lower, and particularly for the Southeast Loch sediments where critical shear stress was about half the value observed at other locations. Erosion rate characteristics were similar for the Paleta Creek stations and the Bishop Point station, but at the Southeast Loch station, smaller applied excess shear stress resulted in larger erosion rates, and the erosion rate increased less dramatically with higher applied excess shear. In general, very low current speeds were observed at both demonstration sites. At the Paleta stations, some short-term, high-current events were observed and are believed to be related to ship and tug movements in the area. Based on these current velocities, the calculated bottom shear at Paleta Creek stations was generally very low during the majority of the measurement conditions. During the suspected ship movement events at Paleta Creek, shear stresses at both sites significantly exceeded critical shear stress. These higher energy events were not detected during the Pearl Harbor deployments, but it is likely they do occur. Where erosion was predicted to occur, the flux of a contaminant depends on the concentration gradient between the mixed layer and the deep layer. Metal concentrations in both layers were generally higher at

the Pearl Harbor stations, with the exceptions of Cd and Ag. Vertical gradients varied across stations and sites, with generally higher concentrations in the deeper sediments at P04 and SL, minimal difference at BP (except Cu), and higher concentrations in the surface layer for P17, particularly for Cu and Zn. PAH concentrations in both layers were generally higher at the Pearl Harbor stations. Vertical gradients varied across stations and sites, with generally higher concentrations in the shallower sediments at P04, P17, and SL, and minimal difference at BP. At both sites, the flux associated with erosion was at most times negligible, at least under the conditions represented by the current meter deployments, except during ship movements. The results indicate that at P04, the concentration of several metals (Cu, Pb, Ni, Zn) increase as the mixed layer erodes as a result of higher concentration of metals in the deep layer. At P17 the opposite occurs, particularly for Cu and Zn. Potential for erosive fluxes at the Pearl sites based on the Paleta erosion rates indicate that erosion could result in significant mass loss of metals from the surface sediments at BP, particularly for Cu and Zn. This should be viewed as an erosion potential, since as previously mentioned, the measured shear stress never exceeded the critical shear. For PAHs, the erosion flux at Paleta Creek stations generally resulted in an decrease in the mixed layer concentration. Potential for erosive fluxes at the Pearl sites based on the Paleta erosion rates indicate that erosion could result in significant mass loss of PAHs from the surface sediments at BP, and particularly for SL.

For both sites, the magnitude of pathway fluxes for arsenic followed a pattern of Advection=Settling>Diffusion>Erosion. Pathway analysis for arsenic indicates that dissolved contaminant processes (advection and diffusion) are leading to a loss of arsenic in the surface layer at both sites, with the exception of advection at BP. However, the sites show opposing patterns for sedimentation with mass loss at the Pearl Harbor sites, and mass gain to the surface layer for the Paleta Creek sites. The magnitude of pathway fluxes for copper indicated a pattern dominated by settling fluxes. Fluxes associated with advection, diffusion and erosion were all negligible relative to settling. At Paleta Creek, settling fluxes at both stations suggest mass gain of Copper in the surface mixed layer, while for Pearl, SL showed a mass gain and BP showed a mass loss due to settling. An examination of all fluxes suggests that the surface mixed layer may be experiencing a net gain of Copper as the sum of all processes at all areas except Bishop Point, with the flux dominated by settling. This pattern is consistent with ongoing activities in the Paleta Creek and Southeast Loch areas including use of antifouling coatings, shipyard operations, and stormwater discharges. These sources are not present to the same degree at Bishop Point.

Pathway analysis for cadmium indicates that dissolved contaminant processes (advection and diffusion) are generally leading to a loss of Cd in the surface layer at both sites, although the variability is very high, especially for diffusion. The advection pathway at Pearl Harbor was negligible relative to Paleta. At Pearl Harbor, settling fluxes at both stations suggest mass loss of cadmium in the surface mixed layer, while for Paleta, P04 showed a mass loss and P17 showed a mass gain due to settling. An examination of all fluxes suggests that the surface mixed layer at both sites may be experiencing a net loss of cadmium as the sum of all processes, dominated by settling, with the exception of Paleta station P17 where results suggest a net gain dominated by settling. This difference at P17 is related to the station proximity to the mouth of Paleta Creek and associated release from storm events. Lead fluxes associated with advection, diffusion and erosion were all negligible relative to settling. Settling fluxes for lead at Paleta Creek are acting

as a continuing source to the surface layer, while at Pearl Harbor they are driving a mass loss from the surface layer. An examination of all fluxes suggests that the surface mixed layer may be experiencing a net gain of lead as the sum of all processes at Paleta Creek areas, and a net loss of lead at Pearl harbor areas, with the fluxes at both sites dominated by settling. This pattern is consistent with ongoing stormwater sources in the Paleta Creek area. It appears these sources are not as prevalent at the Pearl Harbor sites.

Diffusive fluxes of nickel at the two sites were of comparable magnitude and generally indicate mass loss of nickel from the surface layer. Advective fluxes at Pearl Harbor were significantly higher in magnitude and appear to act as a source to the surface layer, in contrast to Paleta Creek where these fluxes generally indicate a mass loss from the surface sediments. Differences in advective fluxes at the two sites could be linked to different approaches for determining the deep layer porewater concentration that were used. Settling fluxes showed the opposite pattern as advective fluxes, with settling leading to mass loss in the surface sediments at Paleta Creek and mass gain in the surface sediments at Pearl Harbor. An examination of all fluxes suggests that Ni concentrations in the surface layer may be near steady state, with Paleta Creek sediments balanced by losses from advection and diffusion and gain from settling, and Pearl harbor sediments balanced by gain from advection and loss from diffusion and settling.

Pathway analysis for silver indicates that variations in surface layer concentrations at both sites are strongly dominated by settling fluxes. Fluxes associated with advection, diffusion and erosion were generally negligible relative to settling, except at P17. Settling fluxes showed no clear pattern between the two sites, with both positive and negative mean fluxes at both harbors. Results suggest settling is an ongoing source of silver to the surface sediments at P04 and Bishop Point, as opposed to Southeast Loch where the settling acts to reduce silver in the surface layer, and P17 where the settling flux is relatively small. An examination of all fluxes suggests that the surface mixed layer response for silver showed no clear pattern across sites, with net gain, net loss, or near steady state conditions occurring at various stations. The net loss or near steady state conditions observed at P17 and Southeast Loch are interesting from the standpoint that these areas are generally closer to industrial and non-point sources than the other two sites. This difference may indicate that the net gain of silver at P04 and Bishop Point results from transport from other areas as opposed to local sources.

Pathway analysis for zinc indicates that dissolved contaminant processes (advection and diffusion) are generally leading to a loss of zinc in the surface layer at both sites. The advection and diffusion pathways were generally stronger at Pearl Harbor relative to Paleta. At Paleta Creek, settling fluxes at both stations suggest mass gain of zinc in the surface mixed layer, while for Pearl Harbor, Bishop Point showed a mass loss and Southeast Loch showed a mass gain due to settling. This pattern is similar to the pattern observed for copper, and these are metals that commonly co-occur in both industrial sources and non-point source. An examination of all fluxes suggests that the surface mixed layer may be experiencing a net gain of zinc as the sum of all processes at all areas except Bishop Point, with the flux dominated by settling. This pattern is consistent with ongoing activities in the Paleta Creek and Southeast Loch areas including use of antifouling coatings, shipyard operations, and stormwater discharges. These sources are not present to the same degree at Bishop Point.

Cross-site comparison for the two demo was evaluated based on comparison of the site-average degradation flux rates for both the depth-integrated assumption and the surface layer assumption. In general, both sites showed a similar pattern in terms of the magnitude of the flux with P>F>N. Depth-integrated mineralization fluxes were generally an order of magnitude higher than near surface fluxes. Fluxes at the Pearl Harbor stations were generally higher than those at Paleta Creek, with the exception of Fluoranthene which was higher at P04. This is consistent with the generally higher level of PAHs present in Pearl Harbor. When the sites and stations are further compared, elevated measured bacterial mineralization of the PAHs naphthalene, phenanthrene, and fluoranthene were found to associate with areas of the sediment that appear to be more bioturbated based on analyses using the SPI camera and microprofiler data (i.e. P04 and SL).

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## **4 References**

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